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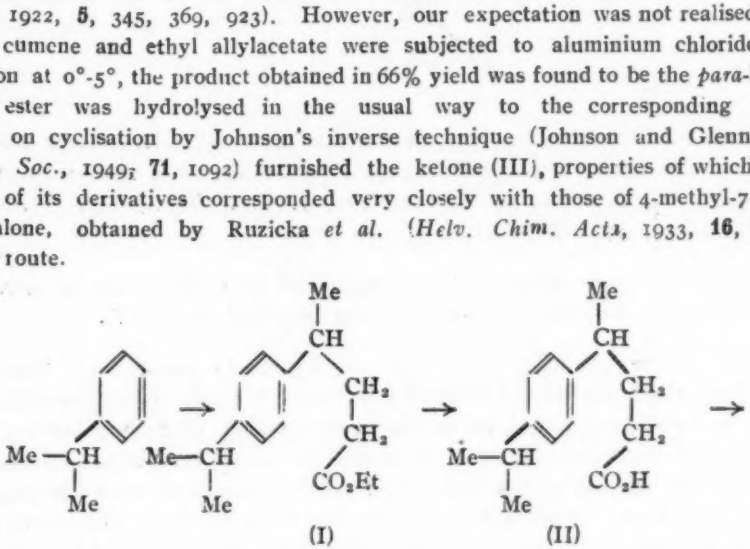
[Jour. Indian Chem. Soc., Vol. 34, No. 1, 1957]

FRIEDEL-CRAFTS' REACTION INVOLVING UNSATURATED KETONES AND ESTERS. PART V. ALKYLATION OF CUMENE AND *p*-CYMENE WITH ETHYL ALLYLACETATE AND ALLYLACETONE

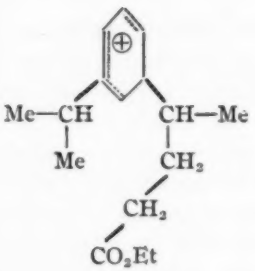
By S. M. Mukherji, O. P. Vig, N. K. Maheswary and Sarjit Singh Sandhu

The Friedel-Crafts alkylation of cumene and *p*-cymene with ethyl allylacetate and allylacetone leads respectively to the *p*-oriented products and *p*-cymyl-2 derivatives. These products prove to be useful intermediates in the elegant synthesis of a variety of naphthalene derivatives.

In view of our experience with toluene, which on the Friedel-Crafts alkylation with ethyl allylacetate and allylacetone afforded the *meta*-oriented products (*J. Org. Chem.*, 1953, **18**, 1499), it was reasonably expected that cumene on similar treatment with ethyl allylacetate would give rise to ethyl 4-(*m*-cumyl)-valerate, which would form an elegant pathway to eudalene, the well-known naphthalene derivative obtained on dehydrogenation of sesquiterpenes of eudesmol group (Ruzicka *et al.*, *Helv. Chim. Acta*, 1922, **5**, 345, 369, 923). However, our expectation was not realised, because when cumene and ethyl allylacetate were subjected to aluminium chloride-catalysed reaction at 0°-5°, the product obtained in 66% yield was found to be the *para*-isomer (I). This ester was hydrolysed in the usual way to the corresponding acid (II), which on cyclisation by Johnson's inverse technique (Johnson and Glenn, *J. Amer. Chem. Soc.*, 1949; **71**, 1092) furnished the ketone (III), properties of which as well as those of its derivatives corresponded very closely with those of 4-methyl-7-*isopropyl*-1-tetralone, obtained by Ruzicka *et al.* (*Helv. Chim. Acta*, 1933, **16**, 269) by a longer route.



That the product (I) was the *para*-isomer was further proved by alkaline permanganate oxidation of the acid (II) to the exclusive oxidation product, terephthalic acid, identified as its *S*-benzyl*iso*thiouronium derivative. No trace of phthalic or *iso*phthalic acid could be detected. The *para*-orientation in the case of cumene is rather intriguing when contrasted with the *meta*-orientation with toluene. It is, however, evident that although the alkylating carbonium ion is the same, the alkyl group (*iso*propyl) already present in the case of cumene is much larger than the methyl group in toluene. As a consequence, the steric interference between the alkylating group and the existing *iso*propyl group within the *meta*- oriented carbonium ion intermediate (VI) will be much greater.

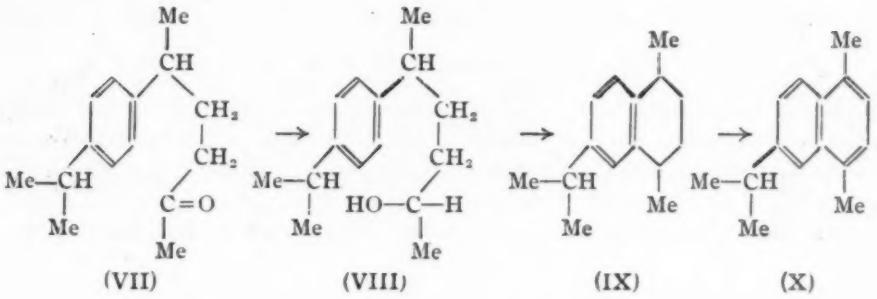


Thus, *para*-orientation in this case, in contrast to *meta*-condensation in the case of toluene, can be reasonably explained on the basis of the steric hindrance involved in the process (cf. Hennion, Driesch and Dee, *J. Org. Chem.*, 1952, **17**, 1102 ; Mukherji *et al.*, *ibid.*, 1954, **19**, 328).

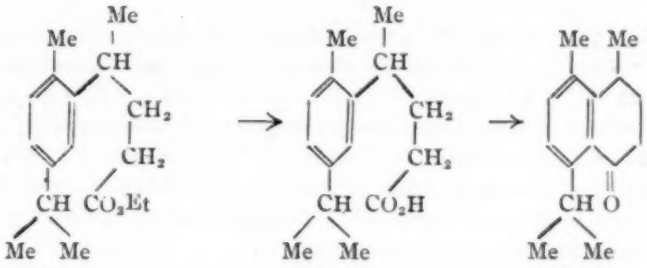
The ketone (III) was reduced (Clemmensen) and the resulting tetralin derivative (IV) dehydrogenated with sulphur to 1-methyl-6-*iso*propylnaphthalene (V).

Similarly, cumene was acted upon with allylacetone in presence of aluminium chloride, when 5-(*p*-cumyl)-hexan-2-one (VII) was obtained in 40% yield. The assignment of the *para*-orientation in the above product (VII) was based on its hypoiodite oxidation to the acid (II). The identity of the two samples of (II) was established by the melting points and mixed melting points of their *S*-benzyl*iso*-thiouronium derivatives. The ketone (VII) was reduced with sodium and moist ether to the carbinol (VIII) which on cyclisation with H_2SO_4 (conc.) furnished the tetralin derivative (IX). Dehydrogenation of (IX) with sulphur afforded a good yield of 1 : 4-dimethyl-6-*iso*propylnaphthalene (X), previously synthesised by Ruzicka *et al.* (*Helv. Chim. Acta*, 1932, **15**, 140 ; 1936, **19**, 370) by a much longer route.

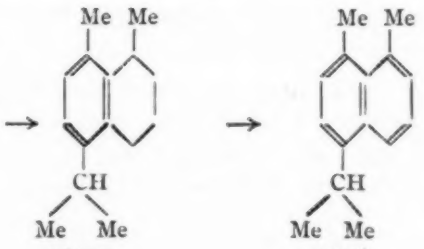
p-Cymene was then studied under a similar sequence of reactions. When subjected to the Friedel-Crafts alkylation reaction with ethyl allylacetate under our standard condition, it gave ethyl 4-(2′-methyl-5′-*iso*propylphenyl)-valerate (XI) in 58% yield.



(VII) (VIII) (IX) (X)



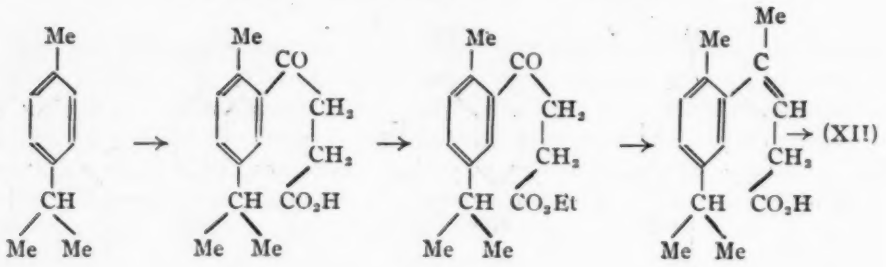
(XI) (XII) (XIII)



(XIV) (XV)

The electrophilic attack at the 2-position of the *p*-cymene molecule is in agreement with the findings of the earlier workers (Le Févre, *J. Chem. Soc.*, 1933, 977, 980), although substitution should have taken place at the 3-position according to the accepted order of inductive effect of alkyl groups. This reverse order in the electrophilic attack has been ascribed by Ganguly and Le Févre (*ibid.*, 1934, 848, 852) to the steric repulsion due to the increasing size of the alkyl group (cf. Hennion, Driesch and Dee, *loc. cit.*). On the other hand, consideration of the well-known no-bond resonance (hyperconjugation) possibilities (Baker and Nathan, *J. Chem. Soc.*, 1935, 1844) suggests that the position *ortho* to the methyl group should be more susceptible to electrophilic attack, as found in the present work, than the position *ortho* to the *iso*propyl group.

The ester (XI) was hydrolysed to the corresponding acid (XII). The point of attachment of the valeric acid moiety was proved by an alternative synthesis of the acid (XII) according to the following scheme :

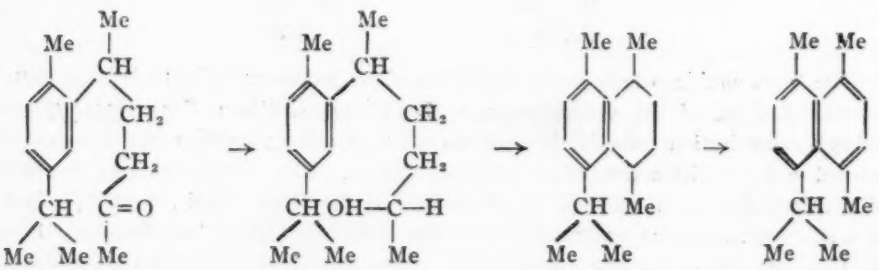


(XX) (XXI) (XXII)

3-(*p*-Cymoyl-2′)-propionic acid (XX) was prepared by reacting *p*-cymene with succinic anhydride in presence of aluminium chloride in nitrobenzene (Guha and Dev, this *Journal*, 1948, **25**, 13). The keto-acid (XX) was esterified and the ester (XXI) acted upon with one molecular proportion of methylmagnesium iodide, when the unsaturated acid (XXII) and/or the corresponding γ-lactone (?) was obtained in 81% yield, which on reduction with red phosphorus and hydriodic acid furnished the acid (XII). The identity of the two samples of the acid (XII) was established by the m. p. and mixed m. p. of their *S*-benzyl*iso*thiouronium derivatives.

The acid (XII) was then cyclised, as described earlier, and the resulting tetralone (XIII) reduced (Clemmensen) and dehydrogenated with sulphur to obtain 1 : 8-dimethyl-4-*iso*propylnaphthalene (XV) in a good yield.

Similarly, *p*-cymene on reaction with allylacetone furnished 5-(2′-methyl-5′-*iso*-propylphenyl)-hexan-2-one (XVI) in 44% yield. This ketone was oxidised by sodium hypoiodite to the acid (XII), proving thereby that the Friedel-Crafts alkylation had taken place at a position *ortho* to the methyl group in *p*-cymene.



(XVI) (XVII) (XVIII) (XXIX)

By following the same sequence of reactions with the ketone (XVI) as in the case of cumene series, namely, reduction (sodium and moist ether), cyclisation (sulphuric acid) and dehydrogenation (sulphur), 1 : 4 : 8-trimethyl-5-*iso*propylnaphthalene (XIX) was obtained in a satisfactory overall yield.

EXPERIMENTAL*

(WITH N. K. MAHESHWARY)

Ethyl 4-(p-*Cumyl*)-*valerate* (I).—Cumene (75 c.c.) was subjected to aluminium chloride-catalysed reaction with ethyl allylacetate (25 g.) and anhydrous aluminium chloride (52 g.), exactly according to the conditions laid down for the reaction with toluene (*J. Org. Chem.*, 1953, **18**, 1499). After working up in the usual way 32 g. (66%) of (I) was obtained, b.p. 160-62°/10 mm. (Found: C, 77.61; H, 9.53. $C_{16}H_{24}O_2$ requires C, 77.37; H, 9.74%).

4-(p-*Cumyl*)-*valeric Acid* (II).—The ester (I: 16 g.) was hydrolysed with alcoholic KOH (10 g. in 10 c.c. water and 220 c.c. alcohol) by refluxing for 13 hours, and then the hydrolysate was worked up in the usual way to give 12 g. (84%) of the acid (II) as a colorless mobile liquid, b p. 161-65°/5 mm. (Found: C, 75.94 H, 9.20. $C_{14}H_{20}O$ requires C, 76.32; H, 9.15%).

The S-*benzylisothiouronium* derivative was prepared in the usual manner (Vogel, "Practical Organic Chemistry", Longman, 1948, p. 738) and was crystallised from dilute alcohol, m. p. 125°. (Found: N, 7.22. $C_{22}H_{30}O_2N_2S$ requires N, 7.05%).

4-*Methyl*-7-iso*propyl*-1-*tetralone* (III).—The acid (II: 11.5 g.) was cyclised in the same manner as in the case of 4-(*m*-tolyl)-valeric acid (*J. Org. Chem.*, 1953, **18**, 1499), using 13.8 g. of PCl_5, to yield 8 g. (76%) of the tetralone (III), b.p. 146-48°/20 mm., as a colorless oil. (Found: C, 83.32; H, 8.87. Calc. for $C_{14}H_{18}O$: C, 83.12; H, 8.97%).

The *semicarbazone* of (III) was prepared in the usual way and was crystallised from ethanol, m.p. 175-76° (Ruzicka *et al.*, *loc. cit.*, record m.p. 176° decomp.). (Found: N, 16.60. Calc. for $C_{15}H_{21}ON_3$: N, 16.21%).

The 2:4-*dinitrophenylhydrazone* was prepared by the sulphuric acid method and was crystallised from ethyl acetate, m. p. 146-47°. (Found: N, 14.50. $C_{20}H_{22}O_4N_4$ requires N, 14.65%).

1-*Methyl*-6-iso*propyltetralin* (IV).—The ketone (III: 8 g.) was refluxed with amalgamated zinc (18 g.), HCl (conc., 30 c.c.), water (14 c.c.), toluene (25 c.c.) and acetic acid (1 c.c.) for 36 hours in an oil-bath at 120°-140°. After every six hours 5 c.c of HCl was added. The reaction mixture was worked up in the usual way and yielded 5.5 g. (74%) of the tetralin (IV), b.p. 154-56°/9 mm. (Found: C, 89.43; H, 10.43. $C_{14}H_{20}$ requires C, 89.29; H, 10.71%).

1-*Methyl*-6-iso*propylnaphthalene* (V).—The tetralin derivative (IV: 5 g.) was heated with sulphur (2.1 g.) at 180° for about 6 hours and then steam-distilled. The distillate was extracted with ether and the ethereal extract cleared with anhydrous sodium sulphate. Fractionation gave 3.1 g. (66%) of the desired product (V), b. p. 117-20°/7 mm. (Found: C, 90.96; H, 8.92. $C_{14}H_{16}$ requires C, 91.25; H, 8.75%).

The *picrate* was prepared in the usual way and was crystallised from alcohol as orange needles, m.p. 148°. (Found: N, 10.30. $C_{20}H_{19}O_7N_3$ requires N, 10.16%).

Oxidation of 4-(p-*Cumyl*)-*valeric Acid* (II).—The acid (II: 1 g.) was oxidised by alkaline permanganate solution (prepared from 30 g. of $KMnO_4$, 600 c.c. water and 2

* Melting and boiling points are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford.

pellets of NaOH) by refluxing for 12 hours. The manganese dioxide was filtered off and the filtrate evaporated to a small bulk and then acidified, when 0.4 g. of terephthalic acid was obtained. The *S*-benzyl*iso*thiouronium derivative of the acid was prepared in the usual manner, m. p. 202-203° (Vogel, *loc. cit.*, reports m.p. 204°).

5-(p-*Cumyl*)-*hexan*-2-*one* (VII).—Cumene (80 c.c.) was subjected to the $AlCl_3$-catalysed reaction with allylacetone (20 g.) and $AlCl_3$ (anhyd., 42 g.) exactly as in the case of (I), when 17 g. (40%) of the ketone (VII) was obtained, b. p. 145-48°/8 mm. (Found: C, 82.63; H, 10.00. $C_{15}H_{22}O$ requires C, 82.5; H, 10.16%).

The *semicarbazone*, prepared in the usual way, was crystallised from dilute alcohol, m. p. 81-82°. (Found: N, 15.12. $C_{16}H_{23}ON_3$ requires N, 15.27%).

5-(p-*Cumyl*) *hexan*-2-*ol* (VIII).—To a solution of the above ketone (VII: 14 g.) in moist ether (120 c.c.) were added gradually small pieces of sodium (20 g.). Whenever the reaction subsided 1-2 c.c. of water was added. After the whole amount of sodium had been consumed, the mixture was worked up in the usual way, when 9 g. (63%) of the alcohol (VIII) was obtained as a colorless oil, b.p. 160-63°/8 mm. (Found: C, 81.35; H, 10.74. $C_{15}H_{24}O$ requires C, 81.76; H, 10.98%).

1:4-*Dimethyl*-6-iso*propyltetralin* (IX).—The above carbinol (VIII) was treated in the cold with ice-cooled H_2SO_4 (10 c.c., *d* 1.84) which was added gradually with shaking for 20 minutes. The contents were allowed to attain the room temperature and then decomposed with ice and worked up in the usual manner, when the tetralin derivative (IX) was obtained in 71% yield (5.9 g.), b. p. 131-34°/10 mm. (Found: C, 89.00; H, 10.84. $C_{15}H_{22}$ requires C. 89.04; H, 10.96%).

1:4-*Dimethyl*-6-iso*propylnaphthalene* (X).—The above tetralin (4 g.) was dehydrogenated with sulphur (1.6 g.) and worked up in the way as in the case of (IV), when 3 g. of 1:4-dimethyl-6 *iso*propylnaphthalene (X) was obtained, b.p. 136-37°/9 mm. (Found: C, 90.45; H, 8.96. Calc. for $C_{15}H_{18}$: C, 90.85; H, 9.15%).

The *picrate* was prepared by the usual method and was crystallised from ethanol as deep yellow needles, m. p. 102-103° (Ruzicka *et al.*, *Helv. Chim. Acta*, 1932, **15**, 140; 1936, **19**, 370, report m. p. 103°). (Found: N, 10.10. Calc. for $C_{21}H_{21}O_7N_3$: N, 9.83%).

Oxidation of 5-(p-*Cumyl*)-*hexan*-2-*one with Sodium Hypoiodite*.—The ketone (VII: 3 g.) was dissolved in dioxane (60 c.c.) and 10% NaOH solution (80 c.c.). The mixture was well stirred and some iodine solution (prepared in the ratio of $KI : I : H_2O = 2 : 1 : 4$) was added when a yellow colour developed. The addition of iodine solution was continued till the dark red colour of iodine persisted in the cold as well as on warming on the water-bath (60°) for 2 to 3 minutes. The excess of iodine was removed by adding a few drops of dilute NaOH solution. The reaction mixture was then allowed to stand when iodoform separated at the bottom. The aqueous layer was decanted and extracted with ether to remove any unchanged ketone. The aqueous layer was acidified with H_2SO_4 (dil.) and the liberated iodine colour discharged with sodium thiosulphate solution. The oily organic layer was taken up in ether, washed and dried (Na_2SO_4). On removal of the solvent the residue gave on distillation under reduced pressure 1.65 g. of the acid (II), b. p. 158-60°/5 mm.

The S-*benzylisothiouronium* derivative was prepared in the usual way and crystallised from alcohol, m.p. 124-25°, undepressed when mixed with the corresponding derivative, previously prepared from (II).

(WITH SARJIT SINGH SANDHU)

Ethyl 4-(2'-*Methyl*-5'-iso*propylphenyl*)-*valerate* (XI).—*p*-Cymene (100 c.c.) was subjected to the cationoid reaction with ethyl allylacetate (15 g.) and anhydrous $AlCl_3$ (30 g.), following exactly the conditions laid down for (I), and the reaction mixture on being worked up in the same manner yielded 18 g. (58%) of the ester (XI), b. p. 145-48°/8 mm. (Found: C, 77.43; H, 10.12. $C_{17}H_{21}O_2$ requires C, 77.82; H, 9.99%).

4-(2'-*Methyl*-5'-iso*propylphenyl*)-*valeric Acid* (XII).—The above ester (18 g.) was refluxed with alcoholic KOH solution (2 g. in 5 c.c. water and 200 c.c. ethanol) for about 12 hours. After working up in the usual way the acid (XII) was obtained as a colorless oil, b. p. 172-74°/5 mm. in 81% yield (13 g.). (Found: C, 76.52; H, 9.23. $C_{15}H_{22}O_2$ requires C, 76.88; H, 9.46%).

The S-*benzylisothiouronium* derivative was prepared in the standard manner (Vogel, *loc. cit.*) and was crystallised from alcohol, m. p. 119°. (Found: N, 7.10. $C_{23}H_{32}O_2N_2S$ requires N, 7.03%).

4:5-*Dimethyl*-8-iso*propyl*-1-*tetralone* (XIII).—The above acid (XII: 10 g.) was converted into its acid chloride with PCl_5 (10 g.) and then cyclised with $AlCl_3$ (6.3 g., anhyd.) in the same manner as for (II), when 7 g. (76%) of the ketone (XIII) was obtained, b.p. 128-30°/6 mm. (Found: C, 83.00; H, 9.45. $C_{15}H_{20}O$ requires C, 83.28; H, 10.96%).

The 2:4-*dinitrophenylhydrazone* was prepared by the sulphuric acid method and was crystallised as red needles from ethyl acetate, m. p. 220-21°. (Found: N, 14.30. $C_{21}H_{24}O_4N_4$ requires N, 14.14%).

1:8-*Dimethyl*-5-iso*propyltetralin* (XIV).—The ketone (XIII: 7 g.) was refluxed with a mixture of amalgamated zinc (45 g.), HCl (conc., 70 c.c.), toluene (40 c.c.), acetic acid (2 c.c.) and water (34 c.c.) for 34 hours at 120°-140°. The reaction mixture was worked up in the usual way when 5.3 g. (81%) of the tetralin (XIV) was obtained, b. p. 118-21°/10 mm. (Found: C, 89.10; H, 10.82. $C_{15}H_{22}$ requires C, 89.00; H, 10.96%).

1:8-*Dimethyl*-4 iso*propylnaphthalene* (XV).—The tetralin (XIV: 5 g.) was heated with sulphur (12 g.) at 180° for 6 hours. The reaction mixture was then worked up in the same way as for (V), when 2.8 g. (57%) of the desired product (XV) was obtained, b. p. 125-28°/6 mm. (Found: C, 90.74; H, 8.86. $C_{15}H_{18}$ requires C, 90.85; H, 9.15%).

The *picrate* was prepared in the usual way and was crystallised as deep yellow needles from ethanol, m. p. 146°. (Found: N, 9.68. $C_{21}H_{21}O_7N_3$ requires N, 9.83%).

Ethyl 3-(p-*Cymoyl*-2')-*propionate* (XXI).—3-(*p*-Cymoyl-2')-propionic acid (50 g.), obtained by the procedure of Dev and Guha (*loc. cit.*), was refluxed for 12 hours with absolute alcohol (550 c.c.) and H_2SO_4 (*d* 1.84, 34 c.c.). The mixture was then worked up in the usual manner when 44 g. of the above ester was obtained, b. p. 190-92°/12 mm. (Found: C, 72.96; H, 8.28. $C_{16}H_{22}O_3$ requires C, 73.28; H, 8.40%).

4-Methyl-4-(2′-methyl-5′-isopropylphenyl)-vinylacetic Acid (XXII).—To the above ester (15 g.) in dry ether (200 c.c.) was slowly added methylmagnesium iodide (prepared from 9 g. of MeI, 1.5 g. of Mg and 100 c.c. of dry ether) with shaking and ice-cooling. After standing overnight the reaction mixture was refluxed on the water-bath for 3 hours and was then decomposed with iced HCl, and extracted with ether. The ethereal extract was shaken with four portions of dilute NaOH solution. The combined NaOH extract was heated with norit, filtered and acidified with iced HCl (dil.), and the liberated oil was taken up in ether, the ethereal solution dried and the solvent removed, when 10 g. (81%) of the unsaturated acid was obtained. This acid was unsaturated to bromine in chloroform (cf. Dev, this *Journal*, 1948, **25**, 69). The crude acid was directly treated for reduction without purification.

4-(2′-Methyl-5′-isopropylphenyl)-valeric Acid (XII).—The above unsaturated acid (10 g.) was refluxed with red phosphorus (7 g.) and HI (80 g., *d* 1.7) in an oil-bath at 130°-140° for 15 hours. The reaction mixture was diluted with water and extracted with ether. The ethereal layer was washed with water and then with 5% Na_2CO_3 solution. The alkaline washings were acidified and the liberated oil taken up in ether and dried (Na_2SO_4). On removal of the solvent the residue after distillation afforded 6 g. of a colorless oil, b.p. 166-68°/5 mm., showing no unsaturation to bromine in chloroform. (Found : C, 76.63; N, 9.18. $C_{15}H_{22}O_2$ requires C, 76.88 ; H, 9.46%).

The S-*benzylisothiouronium* derivative of the above sample was prepared in the usual manner and was crystallised from alcohol, m. p. 119°, undepressed on admixture with the corresponding derivative of the acid (XII).

5-(2′-Methyl-5′-isopropylphenyl)-hexan-2-one (XVI).—*p*-Cymene (60 c.c.) was condensed with allylacetone (16 g.) in presence of $AlCl_3$ (32 g.), following exactly the conditions described in the preparation of (I), when 19 g. (43%) of the ketone (XVI) was obtained, coming over at 155-58°/9 mm. (Found : C, 82.58 ; H, 10.52. $C_{16}H_{24}O$ reeequires C, 82.70 : H, 10.41%).

The *semicarbazone*, prepared in the usual manner, was crystallised from dilute alcohol, m.p. 156°. (Found : N, 14.60. $C_{17}H_{27}ON_3$ requires N, 14.53%).

5-(2′-Methyl-5′-isopropylphenyl)-hexan-2-ol (XVII).—The above ketone (XVI : 14 g.) was reduced with sodium (11 g.) and moist ether according to the procedure described earlier. The reduced product was worked up when 11 g. of the carbinol (XVII) was obtained, b. p. 138-42°/5 mm. (Found : C, 81.73 ; H, 11.23. $C_{16}H_{26}O$ requires C, 81.99 ; H, 11.18%).

1 : 4 : 8-Trimethyl-5-isopropyltetralin (XVIII).—The above carbinol (9 g.) was cyclised with H_2SO_4 (*d* 1.84, 9 c.c.) in the same way as for (VIII), when 6 g. of the tetralin (XVIII) was obtained, b. p. 110-14°/4 mm. (Found : C, 89.03; H, 11.24. $C_{16}H_{24}$ requires C, 88.82 ; H, 11.18%).

1 : 4 : 8-Trimethyl-5-isopropylnaphthalene (XIX).—Dehydrogenation of (XVIII : 5 g.) with sulphur (1.7 g.) was effected under the conditions described in the case of (IX), and on similar working up, the reaction mixture gave 3.2 g. of the desired product (XIX), b.p. 130-33°/8 mm. (Found : C, 90.43 ; H, 9.43. $C_{16}H_{20}$ requires C, 90.50; H, 9.52%).

The *picrate* was prepared in the usual way and was crystallised as red plates from alcohol, m. p. 114°. (Found : N, 9.25. $C_{22}H_{23}O_7N_3$ requires N, 9.50%).

Oxidation of the Ketone (XVI) *with Sodium Hypoiodite.*—The ketone (XVI : 3.5 g.) was oxidised with sodium hypoiodite solution in the same way as described for the ketone (VII). After working up in the same manner, 1.9 g. of the acid (XII), b.p. 172-75°/6 mm., was obtained. The S-*benzylisothiouronium* derivative of the above acid was prepared in the usual way and was crystallised from alcohol, m. p. 119° (undepressed on admixture with the sample obtained earlier from the acid, XII).

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FRIEDEL-CRAFTS' REACTION INVOLVING UNSATURATED KETONES AND ESTERS. PART VI. ALKYLATION OF ANISOL WITH ETHYL ALLYLACETATE AND ALLYLACETONE

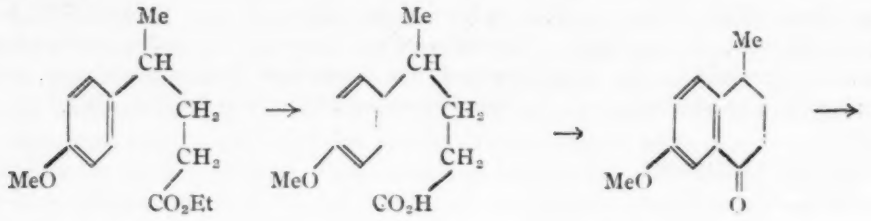
BY S. M. MUKHERJI, O. P. VIG, AND N. K. MAHESHWARY

Cationoid reaction of ethyl allylacetate and allylacetone with anisol has been studied. Of particular interest is the facile cyclodehydration undergone by the condensation product of anisol with allylacetone. Also, the Friedel-Crafts alkylation products proved to be readily accessible intermediates in convenient syntheses of several methoxynaphthalene homologues.

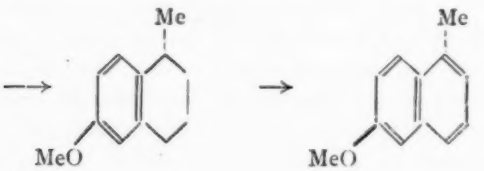
In earlier communications (Mukherji *et al.*, *J. Org. Chem.*, 1952, **17**, 1202 ; 1953, **18**, 1499 ; 1954, **19**, 328 ; this *Journal*, 1955, **32**, 697 ; 1956, **33**, 1), Friedel-Crafts' alkylation of aromatic substrates with ethyl allylacetate and allylacetone was shown to initiate convenient synthetic routes to the different types of polynuclear hydrocarbons. It has now been decided to extend the scope of this method to alkyl aryl ethers. The Friedel-Crafts alkylation of anisol is rather well known (Price, "Organic Reaction", John Wiley, 1949, **3**, 65) and the *para*-orientated products are the preponderant components, although in the case of reaction with *cyclo*hexene (Bodroux, *Ann. chim.*, 1929, *x*, **11**, 511) the *ortho*-isomer is reported to be in greater proportion.

However, when anisol was subjected to aluminium chloride-catalysed reaction at 0°-5° with ethyl allylacetate, 4-(*p*-anisyl)-valerate (I) was the exclusive product obtained in 31% yield. On hydrolysis (I) gave a quantitative yield of the acid (II). That the product (I) was *para*-orientated was proved by alkaline permanganate oxidation of the

acid (II) to *p*-anisic acid ; *o*- or *m*-anisic acid could not be detected. Further, the acid (II) on cyclisation (Johnson and Glenn, *J. Amer. Chem. Soc.*, 1949, **71**, 1092), reduction (Clemmensen) and dehydrogenation with sulphur gave 1-methyl-6-methoxynaphthalene (V).



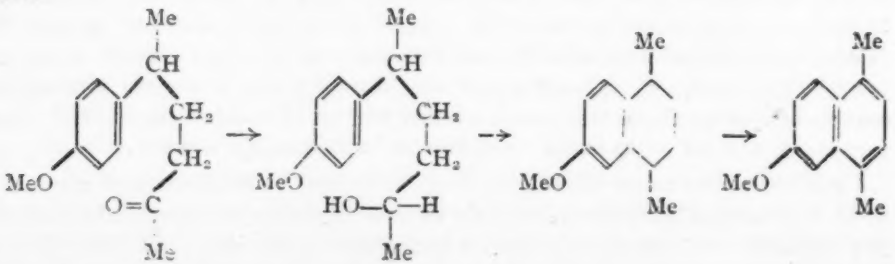
(I) (II) (III)



(IV) (V)

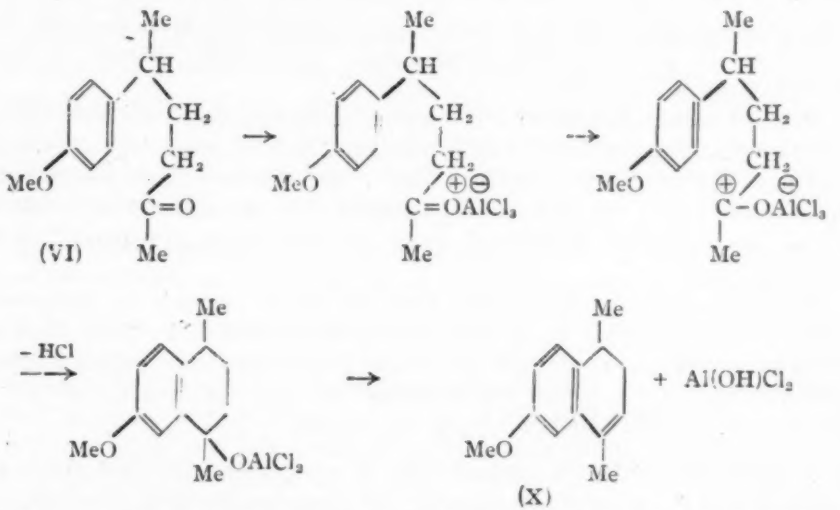
To further improve the yield in the Friedel-Crafts alkylation step, attempts were made to perform this reaction under more drastic conditions of temperature, but extensive methylation resulted in intractable material.

Similarly, anisol was condensed with allylacetone when 5-(*p*-anisyl)-hexan-2-one (VI) was obtained in 31% yield. In the reaction with allylacetone the proportion of aluminium chloride used was less as it was observed that with two moles of this reagent the yield of the ketone (VI) decreased, presumably due to concomitant cyclodehydration (*vide infra*). The orientation was established by sodium hypoiodite oxidation of the ketonic product (VI) to furnish the acid (II), identified through the mixed melting points of the *S*-benzyl*iso*thiouronium derivatives of the two samples of the acid. The ketone (VI) on reduction (sodium and moist ether), followed by cyclisation (sulphuric acid) and dehydrogenation (sulphur), furnished 1 : 4-dimethyl-6-methoxynaphthalene in a good yield.



(VI) (VII) (VIII) (IX)

In one of our experiments with anisol and allylacetone, the temperature rose as high as 50°, and the product obtained failed to afford the semicarbazone. Examination of this product revealed that the initial Friedel-Crafts alkylation was accompanied *in situ* with cyclodehydration to furnish the dihydro derivative (X), which was confirmed by its dehydrogenation with sulphur to 1 : 4-dimethyl-6-methoxynaphthalene (VIII). The formation of (X) may be explained on the basis of initial addition of anisyl group to the double bond of allylacetone, followed by cyclodehydration (cf. Grosse *et al.*, *J. Org. Chem.*, 1938, **3**, 137) according to the following scheme :



The above observation on the facile cyclodehydration of (VI) is very interesting in view of the fact that the *meta* positions with respect to the electron donating methoxy group should, on the contrary, exhibit suppressed anionoid activity as evidenced *inter alia* in intramolecular acylation (Johnson, "Organic Reactions", Wiley, 1949, **2**, 120).

* Experimental

Ethyl 4-(p-Anisyl)-valerate (I).—Freshly distilled anisol (75 c.c.) was allowed to react with ethyl allylacetate (14 g.) in presence of $AlCl_3$ (anhyd., 30 g.) following exactly the procedure recorded by Mukherji *et al.* (*J. Org. Chem.*, 1953, **18**, 1499), and after working up the reaction mixture in the prescribed way, 8 g. (31%) of ethyl 4-(*p*-anisyl)-valerate, b.p. 152-54°/10 mm., was obtained. (Found: C, 71.34; H, 8.49. $C_{14}H_{20}O_3$ requires C, 71.16; H, 8.53%).

4-(p-Anisyl)-valeric Acid (II).—Hydrolysis of the above ester (13 g.) was effected by refluxing it with alcoholic KOH (7.5 g. in 5 c.c. water and 165 c.c. alcohol) on the water-bath for 6 hours. On being worked up in the usual way the hydrolysate furnished 10 g. (87%) of 4-(*p*-anisyl)-valeric acid as a colorless oil, b. p. 171-73°/6 mm. (Found: C, 69.0; H, 7.83. $C_{12}H_{16}O_3$ requires C, 69.21; H, 7.74%).

* Melting and boiling points are uncorrected. Analyses by Drs. Weiler and Strauss, Oxford.

The S-*benzylisothiouronium* derivative was prepared in the usual manner and was crystallised from dilute alcohol, m. p. 125-26°. (Found: N, 7.70. $C_{20}H_{26}O_3N_2S$ requires N, 7.48 %).

4-*Methyl-7-methoxy-1-tetralone* (III).—The acid (II: 10 g.) in dry benzene (20 c.c.) was converted into its acid chloride by PCl_5 (11 g.) in the usual manner and the acid chloride without being isolated was cyclised by aluminium chloride (7.5 g.) according to the conditions described by Mukherji *et al.* (*loc. cit.*) for the preparation of 4·6-dimethyl-1-tetralone, when 4 g. (44%) of the ketone (III), b. p. 102·105°/4 mm., was obtained. (Found: C, 75.62; H, 7.56. $C_{12}H_{14}O_2$ requires C, 75.76; H, 7.42%).

The 2:4-*dinitrophenylhydrazone* was prepared by sulphuric acid method and crystallised as orange-red needles from ethyl acetate, m.p. 215-16°. (Found: N, 15.50. $C_{18}H_{18}O_5N_4$ requires N, 15.15%).

1-*Methyl-6-methoxytetralin* (IV).—The above ketone (III: 3.5 g.) was refluxed with amalgamated zinc (17 g.), toluene (30 c.c.), HCl (conc., 30 c.c.), water (10 c.c.), and glacial acetic acid (1 c.c.) for 36 hours at 120°-130°. The reaction mixture was worked up in the usual way when 2.7 g. of the tetralin derivative (IV) was obtained as a colorless oil, b. p. 120-22°/5 mm. (Found: C, 81.53; H, 9.23. $C_{12}H_{16}O$ requires C, 81.77; H, 9.15 %).

1-*Methyl-6-methoxynaphthalene* (V).—The tetralin (IV: 2.5 g.) was heated with sulphur (1.1 g.) at 180° for about 6 hours and then steam-distilled; the distillate was extracted with ether and the ethereal layer cleared with anhydrous sodium sulphate. Fractionation gave 1.6 g. of the desired product (V), b. p. 135°/10 mm. (Found: C, 83.79; H, 6.93. $C_{12}H_{12}O$ requires C, 83.69; H, 7.02 %).

Oxidation of the Acid (II) *with Alkaline Permanganate.*—The acid (II: 2.5 g.) was refluxed with a solution of $KMnO_4$ (15 g.) and 2 pellets of NaOH in water (300 c.c.) for 8 hours. The manganese dioxide was removed by filtration. The colorless filtrate was evaporated to a small bulk and then acidified with HCl. *p*-Anisic acid (1.2 g.) was obtained as a crystalline precipitate which was recrystallised from water, m. p. 182-83°. Rossel (*Annalen*, 1869, **151**, 30) reported m.p. 184° (decomp.).

5-(*p-Anisyl*)-*hexan-2-one* (VI).—Anisol (100 c. c.) was condensed with allylacetone (20 g.) in presence of $AlCl_3$ (anhyd., 42 g.) at 0°-5° in the way as for (I), when 13 g. (31%) of 5-(*p*-anisyl)-hexan-2-one was obtained, b.p. 136-40°/7 mm. (Found: C, 75.95; H, 8.53. $C_{13}H_{18}O$ requires C, 75.69; H, 8.80 %).

The *semicarbazone* was prepared in the usual way and was crystallised from dilute alcohol, m. p. 151·52°. (Found: N, 15.72. $C_{14}H_{21}O_3N_2$ requires N, 15.96%).

5-(p-*Anisyl*)-*hexan-2-ol* (VII).—The above ketone (6 g.) in moist ether (75 c.c.) was treated with sodium (5.5 g.), added gradually in small pieces with stirring. Whenever the reaction had subsided, 1 c.c. of water was added. After the whole of sodium had been added and consumed, the reaction mixture was washed with water and the ethereal layer dried ($CaCl_2$). Fractionation gave the alcohol (VII) (4.2 g., 68%) as a colorless oil, b. p. 135-36°/4 mm. (Found: C, 74.87; H, 9.32. $C_{13}H_{20}O_2$ requires C, 74.96; H, 9.68 %).

1 : 4-*Dimethyl*-6-*methoxytetralin* (VIII).—The carbinol (VII : 4 g.) was treated in the cold with ice-cooled H_2SO_4 (*d* 1.84, 10 c.c.), added dropwise with shaking for 20 minutes. The mixture was then allowed to attain room temperature and worked up in the usual way, when 2.5 g. of the tetralin (VIII) was obtained, b.p. 195-97°/12 mm. (Found : C, 82 32 ; H, 9.43. $C_{13}H_{18}O$ requires C, 82.06 ; H, 9.54%).

1 : 4-*Dimethyl*-6-*methoxynaphthalene* (IX).—The above tetralin (2 g.) was dehydrogenated with sulphur (0.9 g.) in the same way as described for (V), when 1 g. of (IX), b. p. 156-58°/12 mm., was obtained. (Found : C, 83.94 ; H, 7.32. $C_{13}H_{14}O$ requires C, 83.83 ; H, 7.58 %).

The *picrate* was prepared in the usual manner and was crystallised from ethanol, m. p. 107-108°. (Found : N, 9.70. $C_{19}H_{17}O_8N_3$ requires N, 10.12%).

Oxidation (VI) *with Sodium Hypoiodite*.—The ketone (VI : 3 g.) in dioxan (60 c.c.) was oxidised in the some way as described in Part V (this *issue*, p. 1). The oily product was taken up in ether, washed and dired (Na_2SO_4). Fractionation gave 1.65 g. of 4-(*p*-anisyl)-valeric acid, b.p. 178°/7 mm.

The S-*benzylisothiouronium* derivative, prepared in the prescribed way, was crystallised from ethanol, m.p. 119°, undepressed on admixture with the derivative from (II).

1 : 4-*Dimethyl*-6-*methoxy*-1 : 2-*dihydronaphthalene* (X).—Anisol (50 c. c.) was condensed with allylacetone (10 g.) in the same way as for (I). But after the addition of aluminium chloride (20.8 g.) the ice-bath was removed and the reaction mixture was allowed to acquire the room temperature (25°) and then warmed on the water-bath at 50° for half an hour and then kept standing overnight. After the usual working up, 10 g. (52%) of (X) was obtained, b.p. 194-98°/mm. (Found : C, 83.14 ; H, 8.65. $C_{13}H_{16}O$ requires C, 82.91 ; H, 8.57%).

The above dihydronaphthalene (5 g.) was treated with sulphur (1.04 g.) in the same way as for (IV) and the reaction mixture worked up in the usual manner, when 2.5 g. of the desired product, b.p. 156-60°/12 mm., was obtained. This hydrocarbon was converted into its picrate (5 g.), crystallised from ethanol, m.p. 107°, undepressed when mixed with the picrate of (IX).

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BEHAVIOUR OF CHLORONITROBENZENES WITH HYDRAZINE AND HYDRAZINE DERIVATIVES. PART IV. SOME HALOGENONITROPHENYLHYDRAZINES AND THEIR HYDRAZONES

By Shiam Sunder Joshi and Daleep Singh Deorha

4-Chloro-2 : 6-dinitro-, 4-bromo-2 :6-dinitro-, 3-chloro-2 :4 :6-trinitro-, 6-chloro- 2 :4-dinitro-3-methyl-, 4-bromo-2 : 6-dinitro-3-methyl- and 4-chloro-2 : 6-dinitro-3-methyl-phenylhydrazines have been prepared by replacing a halogen atom by hydrazino group and 2-bromo-5-nitro- and 2-iodo-4-nitrophenylhydrazines have been obtained from the corresponding anilines by diazotisation and subsequent reduction. Some hydrazones have also been prepared.

The present investigation is an extension of the work published in Parts I and II of this series (Joshi and Deorha, this *Journal*, 1951, **28**, 34; 1952, **29**, 46) and includes the preparation of a few more polynitrophenylhydrazines and also of some mononitrophenylhydrazines. Of these, the substituted phenylhydrazines, listed in Table I, have been obtained by the interaction of 1 :4-dichloro-2 :6-dinitro-(Hartley and Cohen, *J. Chem. Soc.*, 1904, **85**, 868), 1 :4-dibromo-2 :6-dinitro-(Jackson and Calhane, *J. Amer. Chem. Soc.*, 1906, **28**, 45), 1 :3-dichloro-2 :4 :6-trinitro-(Sudborough and Picton, *J. Chem. Soc.*, 1906, **89**, 591), 6-chloro-1-bromo-2 :4-dinitro-3-methyl-(Cohen and Smithels, *ibid.*, 1914, **105**, 1509), 1 :4-dibromo-2 :6-dinitro-3-methyl-(Cohen and Dutt, *ibid.*, 1912, **103**, 502), 4-chloro-1-bromo-2 :6-dinitro-3-methyl-(Cohen and Smithels, *loc. cit.*) benzenes respectively with hydrazine hydrate or hydrazine acetate. The halogenomononitrophenylhydrazines could not be prepared like the polynitro compounds ; 2-bromo-5-nitro- and 2-iodo-4-nitro-phenylhydrazines have been obtained by diazotising the corresponding nitroanilines (2-bromo-5-nitro- and 2-iodo-4-nitroanilines) and subsequently reducing the product with sodium sulphite in alkaline medium (Fischer, *Ber.*, 1875, **8**, 589).

The yields of the substituted polynitrophenylhydrazines by the method described earlier (*loc. cit.*, 1951), vary considerably. They are remarkably poor in case of 4-chloro- and 4-bromo-2 :6-dinitrophenylhydrazines, as when the alcoholic solutions of 1 :4-dichloro- and 1 :4-dibromo-2 :6-dinitrobenzenes and hydrazine hydrate are boiled together (even if the proportion of the latter is less), the main products are the hydrazine salts of 6-chloro- and 6-bromo-4-nitro-1-hydroxy-1 :2 :3-benzotriazoles. The triazole formation, however, is avoided to a small extent if the reaction is allowed to proceed by adding small amounts of dilute hydrazine hydrate solution at a time at about 20°. 1 :4-Dibromo- and 4-chloro-1-bromo-2 :6-dinitro-3-methylbenzenes also afford the corresponding hydrazines in poor yields, even on prolonged boiling with hydrazine hydrate solution, as the reactivity of bromine in position-1 in these compounds is comparatively slight though little triazoles are formed in their case.

1 :3-Dichloro-2 :4 :6-trinitrobenzene has two labile chlorine atoms, but only one of them is replaced by the hydrazino group when the alcoholic solution of the compound is boiled with the requisite amount of hydrazine hydrate, and 3-chloro-2 :4 :6-

trinitrophenylhydrazine is formed. The condensation is accompanied with the formation of only a small quantity of the corresponding triazole.

The structure of the hydrazines follows from their methods of preparation. The hydrazones were prepared by the usual methods. They vary in colour from yellow to red. Those from simple carbonyl compounds are often readily soluble in alcohol, while those from aromatic compounds are soluble comparatively less.

Experimental

4-Chloro-2 : 6-dinitrophenylhydrazine.—To a solution of 1 : 4-dichloro-2 : 6 dinitrobenzene in absolute alcohol an equivalent quantity of hydrazine hydrate solution was added in small amounts at a time with vigorous shaking, maintaining the temperature at about 20°, and then left overnight. The substituted hydrazine formed was separated from the triazole salt by repeatedly washing with water and then crystallised from an excess of alcohol.

4-Bromo-2 : 6-dinitrophenylhydrazine was also similarly prepared (Table I). *3-Chloro-2 : 4 : 6-trinitro-, 6-chloro-2 : 4-dinitro-3-methyl-, 4-bromo- and 4-chloro-2 : 6-dinitro-3-methylphenylhydrazines* were all prepared by the method already described (*loc. cit.*, 1951).

2-Bromo-5-nitrophenylhydrazine.—A solution of 2-bromo-5-nitroaniline (5 g.) in excess HCl (dil.) and cooled to about 0° was treated with sodium nitrite (2 g.), dissolved in water (15 c.c.). The product was filtered and the filtrate was slowly added to a cooled solution of sodium sulphite (14 g.) and sodium hydroxide (1.5 g.). After about 30 minutes it was acidified with HCl (conc.), warmed to about 55° and left overnight. The solid separating was boiled with HCl (conc.) and cooled, when crystals of 2-bromo-5-nitrophenylhydrazine hydrochloride separated out. The solid on boiling with water and then treating with sodium acetate gave the free phenylhydrazine, which was crystallised from alcohol.

2-Iodo-4-nitrophenylhydrazine was similarly obtained from 2-iodo-4-nitroaniline.

Characteristics of polynitrophenylhydrazines, prepared as above, are shown in Table I.

Table I

Substituted phenylhydrazines.	Yield.	M.P.	Colour.	Formula.	Halogen. Found.	Halogen. Calc.
1. 4-Chloro-2 : 6-dinitro-	12%	138°	Reddish yellow	$C_6H_3O_4N_4Cl$	Cl, 15.31%	15.25%
2. 4-Bromo-2 : 6-dinitro-	10	142°	Do	$C_6H_3O_4N_4Br$	Br, 28.71	28.88
3. Chloro-2 : 4 : 6-trinitro-	72	176°	Yellow	$C_6H_4O_6N_3Cl$	Cl, 12.47	12.79
4. 6-Chloro-2 : 4-dinitro-3-methyl-	69	201°	Lemon-yellow	$C_7H_7O_4N_4Cl$	Cl, 14.23	14.40
5. 4-Bromo-2 : 6-dinitro-3-methyl-	20	150°	Light orange-red	$C_7H_7O_4N_4Br$	Br, 27.64	27.49
6. 4-Chloro-2 : 6-dinitro-3-methyl-	18	153°	Orange-yellow	$C_7H_7O_4N_4Cl$	Cl, 14.72	14.40
7. 2-Bromo-5-nitro-	72	161°	Yellow	$C_6H_6O_2N_3Br$	Br, 34.26	34.48
8. 2-Iodo-4-nitro-	68	148°	Do	$C_6H_6O_2N_3I$	I, 45.31	45.51

The *phenylhydrazones* were prepared by heating equimolecular quantities of the substituted phenylhydrazines and the carbonyl compounds in alcohol. In case of polynitrophenylhydrazines, a few drops of concentrated sulphuric acid had to be added and heating was done for about 5 minutes, while in the case of mononitrophenylhydrazines, heating for about 20 minutes was necessary. These were crystallised from alcohol; for dinitrophenylhydrazones, however, an excess of alcohol had to be used. Characteristics of the hydrazones prepared are shown in the following tables.

TABLE II

Characteristics of 4-chloro- and 4-bromo-2 : 6-dinitrophenylhydrazones.

Carbonyl compounds.	4-Chloro-.				4-Bromo-.			
	M.P.	Colour.	Chlorine. Found.	Chlorine. Calc.	M.P.	Colour.	Bromine. Found	Bromine. Calc.
1. Formaldehyde	117°	Yellow	14.48%	14.52%	119°	Yellow	27.33%	27.68%
2. Acetaldhyde	108°	Dirty yellow	13.27	13.73	109°	Dirty yellow	26.13	26.40
3. Benzaldehyde	228°	Orange	11.31	11.08	234°	Orange	21.77	21.92
4. Salicylaldehyde	223°		10.27	10.55	221°	Do	21.24	21.00
5. *m*-Hydroxybenzaldehyde	238°	Light violet	10.19	10.55	240°	Light violet	20.87	21.00
6. *p*- do	238°	Orange-red	10.31	10.55	245°	Orange-red	20.84	21.00
7. Anisaldehyde	198°	Red	10.24	10.11	205°	Red	20.09	20.25
8. Cinnamaldehyde	198°	Do	10.07	10.24	209°	Do	20.21	20.43
9. Vanillin	236°	Light violet	9.76	9.68	253°	Light violet	19.30	19.47
10. Heliotropin	240°	Deep red	9.50	9.74	245°	Deep red	19.41	19.57
11. Protocatechuic aldehyde	239°	Dark brown	9.85	10.06	255° (decomp.)	Dark brown	19.99	20.15
12. Acetone	104°	Yellow	13.18	13.02	96°	Yellow	25.15	25.24
13. Methylethyl ketone	132°	Do	12.18	12.39	128°	Orange	24.03	24.18
14. Acetophenone	201°	Orange-red	10.02	10.61	210°	Dark orange-red	21.02	21.11
15. *p*-Methyl-acetophenone	213°	Crimson-red	9.98	10.19	223°	Crimson-red	20.17	20.36
16. Benzophenone	225°	Red	8.89	8.95	233°	Red	17.92	18.14

TABLE III

Characteristics of 3-chloro-2 : 4 : 6-trinitro and of 6-chloro-2 : 4-dinitro-3-methyl-phenylhydrazones.

* Carbonyl compounds.	3-Chloro 2 : 4 : 6-trinitro-.				6-Chloro-2 : 4-dinitro-3-methyl-.			
	M.P.	Colour.	Chlorine.		M.P.	Colour.	Chlorine.	
			Found.	Calc.			Found.	Calc.
1.	152°	Yellow	11.97%	12.26%	216°	Yellowish white	13.51%	13.73%
2.	130°	Orange-yellow	11.33	11.70	120°	Yellow	12.67	13.02
3.	237°	Yellow	9.34	9.71	241°	Do	10.17	10.61
4.	285°	Orange-red	8.87	9.30	245° (decomp.)	Lemon yellow	9.94	10.13
5.	259°	Red	8.88	9.30	284° (decomp.)	Yellow	9.93	10.13
6.	279°	Do	8.81	9.30	249° (decomp.)	Golden yellow	9.87	10.13
7.	240°	Orange	8.34	8.98	229°	Yellow	9.25	9.74
8.	280°	Red	8.87	9.07	194°	Do	9.01	9.85
9.	248°	Do	8.17	8.63	248°	Light orarge-yellow	9.27	9.32
10.	249°	Red	8.44	8.67	221°	Deep yellow	9.01	9.38
11.	279°	Do	8.89	9.14	232°	Orange	9.75	9.69
12.	114°	Yellow	10.93	11.18	111°	Yellow	11.87	12.39
13.	158°	Reddish yellow	10.33	10.71	103°	Do	11.46	11.81
14.	198°	Yellow	9.03	9.35	222°	Do	9.97	10.19
15.	227°	Orange-red	8.89	9.02	216°	Do	9.43	9.79
16.	227°	Red	7.73	8.04	205°	Do	8.23	8.65

* The number of the carbonyl compounds corresponds to those in Table II.

TABLE IV

Characteristics of 4-bromo and 4-chloro-2 : 6-dinitro-3-methylphenylhydrazones.

With 4-bromo-2 : 6-dinitro-3-methyl-					With 4-chloro-2 : 6-dinitro-3-methyl-.				
Carbonyl compounds.	M.P.	Colour.	Bromine.		Carbonyl compounds.	M.P.	Colour.	Chlorine.	
			Found.	Calc.				Found.	Calc.
Benzaldehyde	196°	Orange-red	20.84%	21.11%	Benzaldehyde	199°	Orange-red	10.38%	10.61%
Heliotropin	168°	Red	18.47	18.91	Crotonaldehyde	175°	Red	11 41	11 90
Acetone	102°	Orange-yellow	23.79	24.17	Acetone	106°	Yellow	12.04	12 30
Methylethyl ketone	99°	Do	22.92	23.19	Methylethyl ketone	101°	Orange-yellow	11.40	11 81

TABLE V

Charateristics of 2-bromo- and 2-iodo-4-nitrophenylhydrazones.

* Carbonyl compounds.	2-Bromo-5-nitro-.		Bromine.		2-Iodo-4-nitro-.		Iodine.	
	M.P.	Colour.	Found.	Calc.	M.P.	Colour.	Found.	Calc.
1.	103°	Light yelow	32.34%	32.78%	143°	Light yellow	43.11%	43.64%
2.	110°	Deep yellow	30.94	31.01	135°	Dark brown	41.19	41.64
3.	143°	Orange-yellow	24.67	25.00	157°	Yellow	34.15	34.60
4.	188°	Yellow	23.58	23.81	207°	Dark brown	32.76	33.16
5.	183°	Do	23.51	23.81	228°	Yellowish brown	32.89	33.16
6.	185°	Brown	23.69	23.81	258°	Deep red	32.83	33.16
7.	181°	Red	22.54	22.86	130°	Orange-yellow	31.67	31 99
8.	171°	Deep orange red	22.88	23.12	131°	Orange-red	31.79	32.24
9.	203°	Bright fawn	21.53	21.86	187°	Yellow	30.47	30.75
10.	230°	Orange-yellow	21.79	21.98	208°	Deep yellow	30.71	30.90
11.	234°	Reddish brown	22.54	22.73	242°	Red	31.52	31.83
12.	92°	Yellow	29.10	29.41	112°	Bright yellow	39.64	39 81
13.	76°	Yellowish brown	27.64	27.97	100°	Yellow	37.71	38.15
14.	110°	Yellow	23.72	23.95				
15.	141°	Light orange-yellow	22.73	22.99				
16.	145°	Orange-yellow	19.97	20 20				

* The number of the carbonyl compounds corresponds to those listed in Table II.

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CITRATE COMPLEXES OF LEAD. PART II

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The insoluble lead citrate compound, formed by the neutralisation of a citric acid solution containing lead nitrate, is a dibasic acid. The compound is formed by the action of one of the carboxyl groups and the hydroxyl group of the citric acid, and either a five- or a six- membered ring is formed. This insoluble compound dissolves when the p_H is increased due to the formation of another complex (II) in which three co-ordination positions are occupied by a citrate ligand and, most probably, the fourth position by a molecule of water. This contains a free carboxyl group which ionises, followed by the ionisation of the water molecule, affording complex (III) and complex (IV) respectively. The latter ionisation takes place beyond p_H 9. The formation constants of the complexes (II) and (III) and dissociation constants of complex (II) to (III) and complex (III) to (IV) have been determined.

When a solution of citric acid is mixed with lead nitrate, no precipitate is obtained, and pure lead nitrate can be crystallised from such a mixture by slow evaporation if the solution is concentrated with respect to lead nitrate. When a mixture of citric acid and lead nitrate is treated with sodium hydroxide, a curdy white precipitate is obtained which dissolves on stirring. When further alkali is added, a permanent precipitate is obtained. The amount of the precipitate increases at first with increasing amount of alkali and then decreases and ultimately a clear solution is obtained. If the curdy white precipitate is allowed to stand, it becomes crystalline. These observations appeared interesting and it was thought worthwhile to investigate the system thoroughly.

Kety (*J. Biol. Chem.*, 1942, **142**, 181) has determined the stability constant of lead citrate complex $[PbCit]^-$ by the determination of lead electrode potential. The value of the constant is appreciably variable and has been accounted for as due to the variation of ionic strength. The variation is of the type reported in citrate and gluconate complexes of antimony (Das and Pani, this *Journal*, 1955, **32**, 527 ; Patra and Pani, *ibid.*, 1955, **32**, 572). The variation in the value of the stability constant might be due to the existence of more than one complexes in the solution. Recently, the equilibrium constant of the reaction of lead ion with citric acid has been determined (*J. Chem. Soc., Japan*, 1952, **73**, 92). The reaction is represented by

$$Pb^{2+} + H_3C_6O_7 \rightleftharpoons PbH_3C_6O_7 + 2H^+.$$

The ligand is divalent and the compound is an acid citrate. Nothing has been reported regarding the structure.

From the investigation of the complexes of trivalent antimony with α-hydroxy-acid, it has become clear that the alcoholic group in the α-hydroxy-acid can be induced to react with the cation, if the oxygen-cation bonds have sufficient covalent character. When the cation is attached to one of the oxygen atoms of the carboxyl group by covalent bond, the hydroxyl group in α-position comes sufficiently near the cation, and a covalent bond is formed, if free and stable orbitals are available in the cation.

It is expected that α-hydroxy group of hydroxy-acids would react with divalent lead not only due to similar electronic configuration of divalent lead and trivalent anti-

mony, but there is sufficient evidence to establish that lead-oxygen bonds have appreciable covalent character. Lead ion with three vacant *p* orbitals and a pair of *s* electrons in the outermost quantum level is not expected to behave as divalent barium or strontium ions (divalent lead has ionic radius intermediate between barium and strontium). Though there is some similarity between the properties of divalent lead and barium, the differences are also appreciable. The structure of lead oxide (Moore Jr. and Pauling, *J. Amer. Chem. Soc.*, 1941, **63**, 1392), oxalato-lead complex and acetylacetonate complex of lead indicate directional nature of lead-oxygen bonds, which is an indication of covalent bond. Four orbitals, three *p* and probably one *d* of the same principal quantum level, are used in these compounds. The citrate complexes of divalent lead might be similar to citrate complex of trivalent antimony. Since in the latter, in four co-ordination complexes three *p* and one *d* orbital of the same principal quantum number are most probably utilised. It is therefore worthwhile to investigate the citrate complexes of lead more thoroughly.

EXPERIMENTAL

Insoluble Lead Citrate Compound.—An *M*-citric acid solution (~ 100 c.c.) was mixed with nearly 100 c.c. of *M*/4 lead nitrate solution, and the acid was partially neutralised by adding known amounts of ammonium hydroxide. Three different samples were prepared by adding 25, 50 and 75 c.c. of 2*N* ammonia respectively. The curdy white precipitate obtained was allowed to stand for one day. The crystalline substance obtained was filtered, washed with water, dried at 105° to 110° and analysed for lead content.

The three samples were found to be free of ammonia or ammonium salts, and nitrate. It was therefore assumed that the substance contained lead and citrate. A known amount of the substance (0.2 to 0.3 g.) was dissolved in dilute nitric acid and an excess of potassium chromate was added, followed by a large excess of ammonium acetate solution. The lead chromate was filtered off and chromate content was estimated iodimetrically. The amount of lead was calculated from the amount of chromate. The results are shown in Table I.

TABLE I

Samples.	% Pb found.	% Pb calc. for $PbH_6C_6O_7$.
I	51.71 52.07	
II	51.80 51.98	52.16
III	51.66 51.33	

The results indicate the formulae to be $PbH_6C_6O_7$. Citric acid being tribasic and lead being divalent, at least one of the carboxyl groups of citric acid has not been neutralised in the compound. The compound is expected to behave as an acid.

Basicity of the Insoluble Lead Citrate Compound.—It has been mentioned earlier that the compound dissolves when the p_H is increased by adding alkali. A known amount (0.5 g.) of the substance was suspended in water. A small amount of sodium citrate was added and the mixture was titrated against standard alkali using thymolphthalein as an indicator. Sodium citrate was added to prevent hydrolysis. The results are shown in Table II.

TABLE II

Samples	1	2	3
Wt. of the substance (in g.)	0.4872	0.5064	0.5020
0.1562 *N* NaOH required (in c.c.)	15.65	16.20	16.15
Wt. of substance requiring 2 litres of *N*-NaOH (in g.)	395.9	397.3	395.1

The formula weight of the substance being 397.32, the above results indicate the substance to be a dibasic acid. Two hydrogen ions of citric acid have been replaced due to the formation of the insoluble compound ; two more hydrogen ions cannot be liberated unless the hydroxyl group takes part in the reaction with the liberation of a hydrogen ion. The above observation is further supported by the experiment described below.

A known amount of citric acid was taken and titrated against standard caustic soda using thymolphthalein as an indicator. In another experiment, to the same amount of acid a known amount of a standard lead nitrate solution was added and titrated against the standard NaOH solution. The results are reported in Table III.

TABLE III

Conc. $Pb(NO_3)_2$ = 0.104 *M*. Conc. NaOH = 0.123 *M*. Citric acid taken = 20 c.c.

No.	1	2	3	4
$Pb(NO_3)_2$ added (c.c.)	0.0	0.0	10.0	10.0
NaOH reqd. (c.c.)	60.1	60.1	68.3	68.3

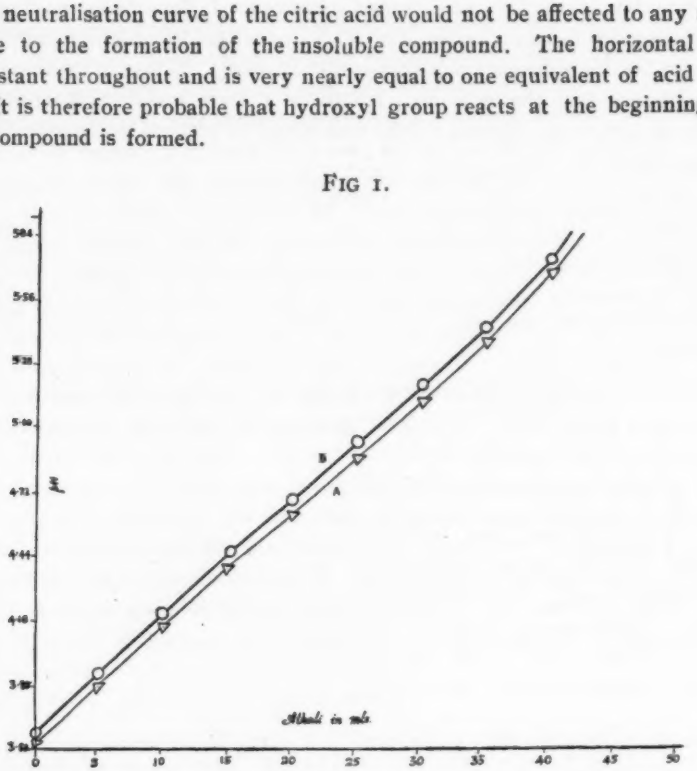
The above results indicate that one equivalent of acid per atom of lead is liberated due to the presence of lead nitrate. For further confirmation of the results, the above experiment was repeated in presence of barium nitrate. But no acid was found to be liberated.

The liberation of hydrogen ion from the hydroxyl group of citrate ligand due to the formation of complex with lead most probably takes place. The above experiments, however, do not establish whether the hydroxyl group reacts when the insoluble compound is formed, or at the time of the soluble complex. Further investigation was carried on as described below.

p_H *Titration.*—Neutralised 0.2*M* citric acid solution (30% ; 125 c.c.) was mixed with 10 c.c. of 0.04836 *M* lead nitrate solution. A precipitate was obtained. The p_H of the solution was measured after the addition of increasing amounts of *N*-NaOH. The results are shown in curve (A) of Fig. 1. In another experiment, the same conditions were maintained except that 10 c.c. of water was added instead of 10 c.c. of lead nitrate. The results are represented by curve (B) of Fig. 1. The horizontal distance between the two curves indicates the amount of acid liberated due to the reaction of lead with citrate. A large amount of citric acid, compared to the amount of lead nitrate, was taken

so that the neutralisation curve of the citric acid would not be affected to any appreciable extent due to the formation of the insoluble compound. The horizontal distance is almost constant throughout and is very nearly equal to one equivalent of acid per atom of lead. It is therefore probable that hydroxyl group reacts at the beginning when the insoluble compound is formed.

FIG 1.



Solubility of the Compound in Partially Neutralised Citric Acid Solution.—The solubility of the compound was determined in partially neutralised citric acid solutions at 35°. In each solvent the concentration of the total citrate was kept constant. The lead contents were determined by precipitating as lead chromate and estimating the chromate iodimetrically. The results are shown in Table IV. It is interesting to note that the solubility of the compound first decreases and then increases with increasing neutralisation of citric acid. The minimum solubility is at about 23 to 24% neutralised solution.

TABLE IV

Conc. of total citrate = 0.5 *M*.

% Neutralisation ...	0.0	10.0	20.0	30.0	60.0
G. moles of $Pb(C_6H_6O_7)$ per litre	0.00393	0.001368	0.0006102	0.001069	0.00362

The higher solubility in pure citric acid is evident from the observation that the insoluble compound is not formed when lead nitrate and citric acid are mixed. The addition of sodium hydroxide to the mixture is tolerated to a certain extent till a permanent precipitate appears. It is therefore expected that the compound would dissolve

to certain extent in citric acid and the solubility would decrease with increasing neutralisation of the acid. The increase in the solubility after the minima is due to the formation of a soluble complex at a higher p_H. If the compound is formed by the action of monohydrogen citrate ion ($HCit^{2-}$) and lead ion, the solubility of the compound would be minimum in 66.6% neutralised solution in which the concentration of $H Cit^{2-}$ is maximum. This is, however, not observed. The minimum solubility is observed in solution in which the concentration of dihydrogen citrate ion ($H_2 Cit^-$) is very high. It is therefore reasonable to assume that the H_2Cit^- ion reacts. The reaction can be represented by equation (1) or (2), depending on whether five- or six-membered ring is formed. It is, however, difficult to say which of the two compounds is actually formed. This compound would be expressed as complex (I) or C.

$$Pb^{2+} + H_2Cit^- \rightleftharpoons H^+ + Pb\begin{cases} O-C=O \\ | \\ O-C-CH_2.COOH \\ | \\ CH_2.COOH \end{cases} \quad \ldots \quad (1)$$

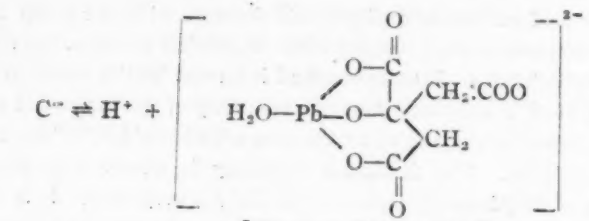
$$Pb^{2+} + H_2Cit^- \rightleftharpoons H^+ + Pb\begin{cases} O-C \\ \| \\ O \\ O-C \\ | \\ HOOC \end{cases} \begin{matrix} \\ \\ CH_2 \\ \\ CH_2.COOH \end{matrix} \quad \ldots \quad (2)$$

The Soluble Lead Citrate Complex.—Complex (I) dissolves when the p_H is increased. The reaction may be represented by equation (3). The co-ordination number of lead in the soluble complex is 4. The three co-ordination positions are occupied by the citrate ligand and the fourth by a molecule of water as in the case of citrate complex of antimony (Das and Pani, *loc.cit.*). (The possibility of four co-ordination complex of lead has been discussed earlier).

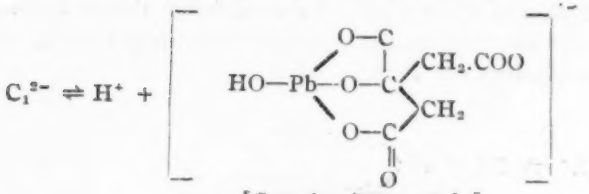
$$C + OH^- \rightleftharpoons \left[\begin{matrix} O \\ \| \\ O-C \\ | \\ H_2O-Pb-O-C \\ \diagdown \quad | \\ O-C \\ \| \\ O \end{matrix} \begin{matrix} \\ \\ CH_2.COOH \\ \\ CH_2 \\ \\ \end{matrix} \right]^- \quad \ldots \quad (3)$$

[Complex (II) or C^-]

The free carboxyl group present in the above complex (II) is first neutralised by a hydroxyl ion and complex (III) is formed. The aquo-complex (III) then dissociates into hydroxo-complex (IV) and hydrogen ion still at a higher p_H. The reactions being



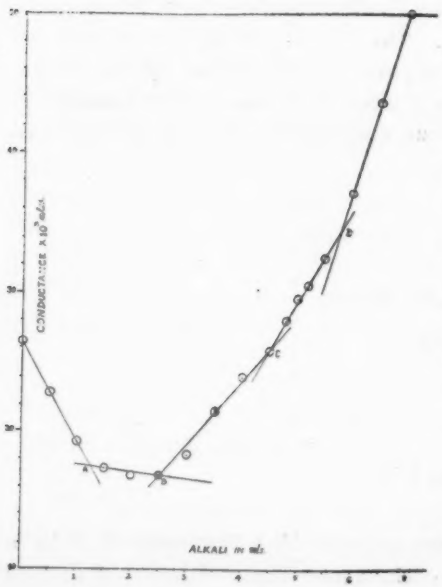
[Complex (III) or C_1^{2-}] ... (4)



[Complex (IV) or C_2^{3-}] ... (5)

Conductometric Titration.—The conductometric titration of a mixture of citric acid and lead nitrate with alkali qualitatively indicates the reactions (1) or (2), (3) and (4). 0.1184 *M*-citric acid (15 c.c.) was mixed with 0.09596 *M* lead nitrate solution (10 c.c.). The mixture was diluted with 300 c.c. of conductivity water. The conductance was measured with a dip type electrode after adding increasing amounts of 1.073 *N*-NaOH solution. The results are graphically shown in Fig. 2.

FIG. 2



The conductance as usual decreases at the beginning due to the neutralisation of fast moving hydrogen ions. When the precipitate is formed, the conductance is very nearly constant (the decrease in conductance is small). Since the amount of hydrogen ion removed by alkali is produced due to the formation of complex (I), the net result of addition of alkali is that, one lead ion and one H_2Cit^- ion are removed and one sodium ion is introduced into the solution. At (B) the reaction (3) commences. For each hydroxyl ion added (the hydroxyl ion is neutralised) a complex (II) is brought and a sodium ion is added to the solution. The conductivity therefore rises. At (C) the whole of the complex (I) is dissolved and the neutralisation of the free carboxyl group of the complex (II) takes place. The p_H rapidly rises and the reaction is complete at (D).

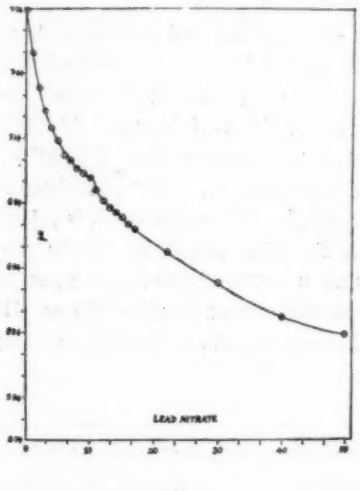
The breaks at (A), (B) and (C) correspond to the beginning of the formation of complex (I), complex (II) and complex (III) respectively. At (D) the formation of the

complex (III) from complex (II) is complete. The formation of complex (IV) is not indicated, since the conductivity of the solution is very high. The formation of the complex (IV) is, however, inferred from the following observations. If sulphuric acid is added to a solution where the condition for the complete formation of the complex (III) is maintained, a white precipitate is immediately obtained. No precipitate is obtained if ammonium sulphate is added. If excess of sodium hydroxide is added, the addition of sulphuric acid does not result in precipitation so long as the excess of sodium hydroxide is not neutralised. The precipitation of lead chromate is also suppressed to a certain extent. The excess of alkali requires neutralisation before any precipitate can be obtained. The added alkali does not appear to be free. Reaction (5) most probable takes place.

Determination of Equilibrium Constant

p_H *Titration Method.*—A solution (75 c.c.) containing 0.004992 g. moles of sodium citrate and 0.025 g. of potassium nitrate was taken and increasing amounts of 0.05*M* lead nitrate solution were added and the p_H of the resulting solution were measured. The results are graphically shown in Fig. 3. Potassium nitrate was added to the system to keep the ionic strength very nearly constant. The curve indicates that acid is liberated due to the reaction, and thus, the p_H of the system is lowered with the increasing amounts of lead nitrate added. The amount of lead nitarte added being less than the amount of sodium citrate, from the results discussed before it can be assumed that the formation of lead citrate complex is almost complete and the concentration of free lead ion is very small and can be neglected, compared to the concentration of the complex. The complex being a soluble one is assumed to be C^-.

FIG. 3



The formation of C^- is complete. Since the p_H of the system is maintained above 7, a portion of the complex dissociates into C_1^{2-} and H^+, and thus, lowers the p_H of the system. The reaction is represented by equation (4) and the equilibrium constant by equation (4-1), where $[C^-]$, $[C_1^{2-}]$ and $[H^+]$ represent the molar concentration of complex C^- complex, C_1^{2-} and H^+ ion respectively.

$$\frac{[C_1^{2-}] \times [H^+]}{[C^-]} = K_1 \qquad \ldots \qquad \ldots \quad (4\text{-}1)$$

The citrate ions (Cit^{3-}) being strongly basic remove the liberated protons with the formation of monohydrogen citrate ion, dihydrogen citrate ion and citric acid. The molar concentration of different ions are represented by square brackets.

$$Cit^{3-} + H^+ \rightleftharpoons HCit^{2-} \quad \ldots \quad (6)$$

$$Cit^{3-} + 2H^+ \rightleftharpoons H_2Cit^- \quad \ldots \quad (6\text{-}1)$$

$$Cit^{3-} + 3H^+ \rightleftharpoons H_3Cit \quad \ldots \quad (6\text{-}2)$$

$$\text{Total acid liberated} = [C_1^{2-}] = [H^+] + [HCit^{2-}] + 2[H_2Cit^-] + 3[H_3Cit]$$

$$\text{or } [C_1^{2-}] - [H^+] = [HCit^{2-}] \times \left(1 + 2\frac{[H^+]}{k_2} + 3\frac{[H^+]^2}{k_1 \times k_2}\right)$$

$$\text{or} \qquad [C_1^{2-}] - [H^+] = a \times [HCit^{2-}] \quad \ldots \quad (7)$$

where k_1 and k_2 are respectively the first and second dissociation constants of citric acid.

$[Ct]$ = total citrate = free citrate + citrate in complex.

$$\text{Free citrate} = [Cit^{3-}] + [HCit^{2-}] + [H_2Cit^-] + [H_3Cit]$$

$$= [HCit^{2-}] \times \left(\frac{k_3}{[H^+]} + 1 + \frac{[H^+]}{k_2} + \frac{[H^+]^2}{k_1 \times k_2}\right)$$

or Free citrate $= b \times [HCit^{2-}]$.

k_3 is the third dissociation constant of citric acid.

Citrate in the complex = total lead nitrate = $[Pb(NO_3)_2]$.

Hence $[Ct] - [Pb(NO_3)_2] = b \times [HCit^{2-}] \quad \ldots \quad (8)$

$[Ct]$ is calculated from the g. moles of sodium citrate added and the total volume. $[Pb(NO_3)_2]$ is also similarly calculated. The total volume and $[H^+]$ are obtained from graph ; "a" and "b" are calculated taking $k_3 = 3.24 \times 10^{-6}$, $k_2 = 4.07 \times 10^{-5}$ and $k_1 = 8.32 \times 10^{-4}$ (Schwarzenbac and Ackermann, *Helv. Chim. Acta*, 1949, **32**, 1682). Substituting the values of $[Ct]$, $[Pb(NO_3)_2]$ and b in equation (8), $[HCit^{2-}]$ is obtained. Substituting the values of $[HCit^{2-}]$ in equation (7), $[C_1^{2-}]$ is obtained. $[C^-]$ is obtained by subtracting $[C_1^{2-}]$ from $[Pb(NO_3)_2]$. The value of K_1 is calculated by equation (4-1). The values are shown in Table V. The values are fairly constant except the last one, and the average value is 8.08×10^{-8}. Since it is not possible to ascertain the concentration of lead ion, the formation constant of complex (II) or (III) from lead ion and citrate ion cannot be calculated. It was therefore decided to adopt the solubility method.

TABLE V

p_H.	$[Ct] \times 10^2$.	$[Pb(NO_3)_2] \times 10^3$.	$[C_1^{2-}] \times 10^3$.	$C^-] 10^3$.	$K_1 \times 10^8$.
7.54	6.569	0.846	0.5728	0.2732	6.04
7.38	6.483	1.362	0.8079	0.5541	6.08
7.28	6.400	1.923	0.9922	0.9308	5.60
7.19	6.320	2.543	1.189	1.345	5.71
7.13	6.240	3.125	1.330	1.795	5.50
7.06	6.163	3.777	1.522	2.255	5.87
6.96	5.873	5.886	1.739	3.848	4.96
6.82	5.672	7.386	2.216	5.170	6.49
6.78	5.557	8.333	2.318	6.015	6.39
6.74	5.487	8.792	2.474	6.254	7.20
6.72	5.426	9.239	2.528	6.711	7.18
6.61	5.146	11.340	2.861	8.479	8.26
6.47	4.754	14.290	3.199	11.090	9.78
6.30	4.341	17.400	3.561	13.840	12.99

Solubility Method.—Lead chromate was prepared from G. R. quality lead nitrate and potassium chromate. It was washed, dried at 105° and analysed for chromate content iodimetrically and found 99.9% pure. The solubility of this sample was studied in sodium citrate and in equimolecular mixture of sodium citrate and sodium hydroxide of various concentrations at 35°. The solubility was obtained by estimating the chromate contents of solutions. The p_H was also measured. The results are recorded in Tables VI and VII respectively for sodium citrate and the mixture of sodium citrate and sodium hydroxide systems.

TABLE VI

$[CrO_4^{2-}] \times 10^4$.	p_H.	[Ct].	$[Pb^{2+}] \times 10^{11}$.	$[Cit^{3-}]$.	$K_2 \times 10^9$.
2.611	8.44	0.25	3.444	0.2497	11.04
2.374	8.48	0.23	3.787	0.2298	9.04
2.232	8.59	0.21	4.029	0.2098	6.79
2.136	8.62	0.20	4.210	0.1998	6.09
1.807	8.64	0.15	4.937	0.1498	5.56
1.519	8.61	0.10	5.917	0.9985	6.32

TABLE VII

$[CrO_4^{2-}] \times 10^4$.	p_H.	[Ct].	$[Cit^{3-}]$.	$[Pb^{2+}] \times 10^{12}$.	K_2.	$[C_1^{2-}] \times 10^4$.	$[C_2^{2-}] \times 10^3$.	$K_3 \times 10^{18}$.
1.229	10.59	0.25	0.2377	0.7821	1.780	5.403	1.1750	5.59
1.120	10.62	0.23	0.2188	0.8035	1.660	5.475	1.0650	4.67
0.8879	10.64	0.21	0.2011	1.014	0.996	6.648	0.8212	2.90
0.8464	10.67	0.20	0.1915	1.063	0.889	7.044	0.7760	2.36
0.8704	10.76	0.15	0.1413	1.034	1.040	6.279	0.8076	2.24
0.6554	10.84	0.10	0.09344	1.373	0.739	6.685	0.5886	1.29

From the p_H titration it is seen that major portion of the complex is in the form of C_1^{2-} at p_H 7.54. The p_H of the solutions of lead chromate in sodium citrate lies between 8.44 and 8.64 and that in equimolecular mixture of sodium citrate and sodium hydroxide between 10.54 and 10.84. It is assumed that in these solutions the concentrations of C^- are very small, and hence, neglected. The solubility of lead chromate being very small, the whole of the lead in the solution is assumed to be present as complex and equal to the concentration of the chromate ion. The concentration of lead ion is obtained by dividing the solubility product of lead chromate (the solubility product at 35° was determined and found to be 1.8×10^{-14}) by the concentration of chromate ion. The concentration of citrate ion was obtained by subtracting the concentration of the complex from total citrate originally taken. The reaction may be represented by

$$Pb^{2+} + Cit^{3-} \rightleftharpoons H^+ + C_1^{2-} \quad \ldots \quad \ldots \quad (9)$$

The equilibrium constant is given by

$$\frac{[C_1^{2-}] \times [H^+]}{[Pb^{2+}] \times [Cit^{3-}]} = K_2 \quad \ldots \quad \ldots \quad (9\text{-}1)$$

The equilibrium constants calculated by equation (9-1) are shown in Tables VI and VII ; the values of K_2 are very nearly constant in each series but vary from one series to the other by a factor of 10. The high value of K_2 in higher p_H series is probably due to the dissociation of the water molecule in the complex C_1^{2-} as assumed in the reaction (5). The equilibrium constant K_3 of the reaction is represented by

$$\frac{[C_2^{3-}] \times [H^+]}{[C_1^{2-}]} = K_3 \quad \ldots \quad (5\text{-}1)$$

Taking K_2 to be 7.47×10^{-2} (the average value in sodium citrate system; Table VI) the values of C_1^{2-} are calculated for the higher p_H series (Table VII). C_2^{3-} is obtained by subtracting $[C_1^{2-}]$ from the total lead. The values, thus calculated, together with K_3 are shown in Table VII, in the last three columns The average value of K_3 is 3.17×10^{-10}. The equilibrium K of the reaction

$$Pb^{2+} + Cit^{3-} \rightleftharpoons C^- \quad \ldots \quad (10)$$

can be obtained by dividing K_2 by K_1 (obtained by the p_H titration method). Thus the value of K is 9.3×10^5.

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THE MOLECULAR POLARISATIONS AND APPARENT DIPOLE MOMENTS OF TITANIUM TETRACHLORIDE, TIN TETRACHLORIDE AND TIN TETRAIODIDE IN NON-POLAR SOLVENTS

By A. R. Tourky and H. A. Rizk

Titanium tetrachloride and tin tetraiodide are found to be non-polar, whereas tin tetrachloride is found to be polar, irrespective of the solvent used. The former two halides apparently possess tetrahedral structures with the metal atom at the centre of the grouping, whereas tin tetrachloride has pyramidal structure with tin at the apex. The total polarisation of each of the three halides at infinite dilution, whether obtained from Debye's or modified equations, varies with the solvent, thus indicating inadequacy of those equations based on modified field theory to account for the effect of the solvent. The ratio of the polarisation at infinite dilution calculated from any modified equation to that calculated from Debye's equation is invariable with the solvent and appears to be higher for a polar than for a non-polar halide. From such calculations it seems likely that substances of near apparent dipole moment values should possess nearly the same ratio.

Tetravalent metal halides are attracting now the attention of many investigators due to their use as starting materials for the production of these metals. It is therefore of theoretical and practical interest to obtain information regarding the structure of these halides. In spite of its importance as an effective tool in elucidating molecular structures, the method of dipole moment has only been scarcely applied to these metal halides, and the results obtained are either varying or fortuitous where agreement has been attained. Tin tetrachloride, for example, was found by Ulich and co-workers(*Z. physikal. Chem.*, 1932, **B17**, 369) to be polar in benzene and non-polar in carbon tetrachloride, whereas Bergmann *et al.* (*ibid.*, 1931, **B13**, 232), who carried out measurements only in carbon tetrachloride, found it to be polar. Although the experimental procedure of the latter authors was criticised by the former ones, they both arrived at the same conclusion in respect of the structure of titanium tetrachloride when using the solvent carbon tetrachloride. These authors applied in their calculations Debye's equation which was then modified by others (Henriquez, *Rec. trav. chim.*, 1935, **54**, 574; Newton, *J. Franklin Inst.*, 1937, **224**, 583; *Trans Faraday Soc.*, 1951, **47**, 1304; Kirkwood, *J. Chem. Phys.*, 1939, **7**, 911) to account for the mutual interaction between molecular dipoles.

The object of the present investigation is to determine the dipole moments of the tetravalent halides: titanium and tin tetrachlorides and tin tetraiodide, by carrying out dielectric constant measurements in non-polar solvents as benzene and carbon tetrachloride, and to examine the feasibility of the assumption of the non-solvent effect by using the modified equations.

EXPERIMENTAL

Chemically pure titanium and tin tetrachlorides were subjected four times to vacuum distillation, following a method similar to that given by Archibald ("The Preparation of Pure Inorganic Substances", New York, 1932, pp. 184, 212). Tin tetraiodide was crystallised thrice from CCl_4, well dried and then subjected to the same treatment as the chlorides. Benzene, CCl_4 and nitrobenzene of "Analar" grade were rigorously dried and purified according to recommended procedures (Weissberger and Proskauer," Organic Solvents, Physical Constants and Methods of Purification", 1935, pp. 105, 107, 163).

Measurements.—The dielectric constant, ϵ, was measured using a resonance circuit in which a frequency of 10^6 cycles per second was fixed by a quartz crystal. The silvered Sayce-Briscoe measuring cell (Le Févre," Dipole Moments", Methuen, 1948, p. 32) could not be applied on account of chemical interaction with the halides, and thus, a specially designed cylindrical platinum cell was used. It was rigidly fixed in a jacket that could be connected to an ultra-thermostat. The air-capacity of the cell was $30\mu\mu F$, the range over which ϵ could be measured was 1.9—3.1 and the volume required to fill the annulus was 8 c.c. In the calibration of the apparatus, only liquids of reliable dielectric constants were used, thus:

	Benzene*†.	*CCl_4.	**Nitrobenzene in benzene.		
ϵ at 25° ...	2.2725	2.2270	2.2925	2.3000	2.3325
			f_2=0.0008707	0.001197	0.002612

*Le Fe'vre, *Trans. Faraday Soc.*, 1938, **34**, 1129.

† Hartshorn *et al.*, *Proc. Roy. Soc.*, 1929, **123A**, 664.

** Le Fèvre *et al.*, *Trans. Faraday Soc.*, 1936, **49**, 1136; Jenkins, *J. Chem. Soc.*, 1934, 482.

The uncertainty in ϵ was $\pm$ 0.0005.

The density was measured by a pyknometer of the Sprengel-Ostwald type that was filled by the method of Smyth and Morgan (*J. Amer. Chem. Soc.*, 1928, **50**, 1547) and Miller (*ibid.*, 1934, **56**, 2360). The refractive index for the Na_D line was directly measured by means of a Hilger-Abbe refractometer. The concentration was determined, using Dorfman and Hildebrand's method (*ibid.*, 1927, **49**, 729). All measurements were made at 25° $\pm$ 0.002°.

The total molecular polarisation of the halide, P_2, at different concentrations was calculated using the modified Clausius-Mosotti-Debye equation (Le Févre, "Dipole Moments", 1948, p. 7; Debye, "Handbuck der Radiologie", 1925, pp. 6, 600). applicable to solutions. The polarisation at infiuite dilution, $P_{2\infty}$, was graphically and mathematically determined. In the latter case, the Hedestrand method (*Z. physikal. Chem.*, 1929, **B2**, 428) and the Palit-Banerjee method (*Trans. Faraday Soc.*, 1951, **47**, 1299) were used. The mean of the values of $P_{2\infty}$, as deduced by the three methods, was then taken. The part of the molecular polarisation arising from induced dipoles, R_2, was calculated from measurements of n_D using the modified form of Lorenz-Lorentz equation (Le Févre, "Dipole Moments," pp. 11, 17) applicable to solutions and then

TABLE I

Solvent.	$t°$.	$P_{2\infty}$ (Debye) (c.c.) Graphical.	Hedestrand.	Palit & Benerjee.	Mean value.	* α.	β†.	P_2 (c.c.).	$_AP_2$ (c.c.).	μ_B. ($\times 10^{18}$).	$P_{2\infty}$ (modified formulae) (c.c.) Henriquez.	Kirkwood.	Newton.	Ref.
					Titanium tetrachloride.									
Benzene	14.7-20.0°	44-45	...	...	...	...	...	37.8	2.70	0	...	...	...	Ulich *et al.*
	25.0°	43.93	44.27	44.09	44.10	0.5611	0.9420	37.10 n_∞	3.71	0	48.32	53.95	68.03	Present authors
CCl_4	15.0-18.0°	40-41	...	...	...	...	...	37.8	2.70	0	...	...	...	Ulich *et al.*
	19.8°	43.2	...	...	...	...	...	43.23	...	0	...	...	...	Bergmann
	25.0°	40.31	40.33	40.34	40.33	0.5591	0.1992	36.86 n_∞	3 69	0	44.02	49 18	62.07	Present authors
					Tin tetrachloride.									
Benzene	14.7-20.0°	58	...	...	...	...	...	35.2 n_∞	8-10	0.80	...	...	...	Ulich *et al.* Present authors
	25.0°	56.65	56.79	56.50	56.64	1.3502	1.7015	34.26 n_∞	3.43	0.96	63.35	72.24	92.88	
CCl_4	15.0-18.0°	43-45	...	...	...	...	...	35.2	8-10	0	...	...	...	Ulich *et al.*
	17.7°	52.5	...	...	...	...	...	n_∞	...	0.80	...	...	...	Bergmann
	25.0°	53 45	53.50	53.32	53.42	1.1453	0.7248	38.91 34.42 n_∞	3.44	0.86	59.31	67.26	86.14	Present authors
					Tin tetraiodide.									
Benzene	25.0°	26.70	...	...	...	...	...	... 24.74	30	0	...	...	...	Williams Allgeier
	25.0°	26.50	26.62	26.84	26.65	0.5967	6.4226	n_∞	2.47	0	29.60	33.67	43.20	Present authors

* $\alpha = \frac{\Delta \epsilon_{12}}{\Delta f_2}$, where ϵ_{12} is the dielectric constant of the solution and f_2 is the mol. fraction of the solute ($\epsilon_{12} = \epsilon_1 + \alpha f_2$).

† $\beta = \frac{\Delta d_{12}}{\Delta f_{12}}$, where d_{12} is the density of the solution ($d_{12} = d_1 + \beta f_2$).

α and β are determined by the method of least squares.

corrected by means of the dispersion formula,

$$\left(1 - \frac{\lambda_0^2}{\lambda^2}\right) R_\lambda,$$

where $\lambda_0 = 1013$Å (Miller, *loc. cit.*) and $\lambda = 5896$Å (Allsopp and Willis, *Proc. Roy. Soc.*, 1936, **153A**, 379) so as to get the molecular refraction for infinite wave-length, $R_{2\infty}$, which is identical with the electronic polarisation ${}_E P_2$. The deformation polarisation, ${}_D P_2$, was taken as 1.10 $R_{2\infty}$ (Zahn and Miles, *Phys. Rev.*, 1928, **32**, 497) and the dipole moment μ was obtained by the refractivity method (Le Févre, *loc. cit.*, p. 12).

The modified formulae of Henriquez, Kirkwood and Newton (vide Smith and Witten, *Trans. Faraday Soc.*, 1951, **47**, 1315) were also used in evaluating the polarisation at infinite dilution for studying the solvent effect. The results obtained are summarised together with those of previous workers in Table I.

Discussion

Titanium Tetrachloride.—The electronic polarisation value is in better agreement with Ulich's value (*loc. cit.*) than with that of Bergmann (*loc. cit.*). The orientation polarisation is zero in CCl_4 and 3.29 c.c. in benzene. Thus, titanium tetrachloride is a dipole-free halide and may be considered as a tetrahedral grouping around Ti in agreement with previous results arrived at by other different methods (Wierl, *Ann. Physik*, 1931, *v*, **8**, 521; Trumpy, *Z. Physik*, 1930, **66**, 790).

Table II

$t = 25°$.

Halide.	Solvent	$P_{2\infty}$ (in c.c.)			
		Kirkwood.	Herniquez.	Newton.	Debye.
$TiCl_4$	C_6H_6	53.95	48.32	68.03	44.10
	CCl_4	49.18	44.02	62.07	40.33
$SnCl_4$	C_6H_6	72.24	63.35	92.88	56.64
	CCl_4	67.26	59.31	86.14	53.42
SnI_4	C_6H_6	33.67	29.60	43.20	26.65

Table III

$t = 25°$.

Halide.	Solvent.	$\frac{P_{2\infty}K}{P_{2\infty}D}$.	$\frac{P_{2\infty}H}{P_{2\infty}D}$.	$\frac{P_{2\infty}N}{P_{2\infty}D}$.	$\mu_R \times 10^{18}$
$TiCl_4$	C_6H_6	1.22	1.09	1.54	0
	CCl_4	1.22	1.09	1.54	0
$SnCl_4$	C_6H_6	1.27	1.11	1.64	0.95
	CCl_4	1.26	1.11	1.61	0.86
SnI_4	C_6H_6	1.27	1.11	1.62	0

Tin Tetrachloride.—The electronic polarisation value is very near to Ulich's value but not appreciably lower than that of Bergmann. The atomic polarisation of this

halide was determined by the former author as the difference between its total polarisation in the solid state and its electronic polarisation; the value obtained being 8-10 c.c. in agreement with 10.8 c.c. obtained by Smyth (*Phil. Mag.*, 1925, **50**, 361) by the same method. Jenkins (*Trans. Faraday Soc.*, 1934, **30**, 739) considering non-existence of atomic polarisations higher than 7 c.c., ascribed those in the neighbourhood of 10 c.c. to the hygroscopic nature of the halide. If, however, the atomic polarisation value due to Ulich were estimated as 10% of the electronic polarisation, a value of 3.52 c.c. would have been obtained, which is as low as our value of 3.43 c.c., determined by the same method. The dipole moment of this halide, when determined in CCl_4, is 0.86 D, thus agreeing with Bergmann's value of 0 80 D and deviating from that of Ulich, which is zero. Although the total polarisation, as determined in CCl_4, is quite comparable with that of Bergmann and higher than that of Ulich, yet it could not be ascribed to the probable presence of water, as was inferred by Ulich when discussing Bergmann's data, firstly because the total polarisation of this halide, when determined in benzene, is found to be very near to that of Ulich, and secondly, because there is no reason to assume that the presence of water would have a detrimental effect greater in CCl_4 than in benzene, since the solubility of HCl in the former solvent is less than that in the latter (Faibrother, *J. Chem. Soc.*, 1932, 43).

The assumption therefore, made by Ulich that tin tetrachloride forms in benzene associate complexes giving rise to the observed orientation term and the absence of such tendency in CCl_4, appears to be unnecessary. This compound may accordingly be conceived to possess a pyramidal structure with Sn located at the apex so as to account for the presence of an electric doublet in the molecule, detectable in the different non-polar solvents.

The higher polarisation values at infinite dilution in benzene than in CCl_4 for the two halides may be attributed to the higher dissociating power of the former solvent (Van Arkel and Snoek, *Rec. trav. chim.*, 1933, **52**, 719). Also by taking into account the properties of the solute besides those of the solvent, Weigle (*Helv. Phys. Acta*, 1933, **6**, 681) concludes that when polarisation measurements of one substance are carried out in different solvents, the solvent with the higher dielectric constant yields greater polarisation value.

Tin Tetraiodide.—Measurements on tin tetraiodide show that this compound is non-polar. This agrees with the previous work carried out by Williams and Allgeier (*J. Amer. Chem. Soc.*, 1927, **49**, 2416) and with the conclusion drawn out by Hildebrand ("Solubility", 1924, Chap. 14; Dorfman and Hildebrand, *loc. cit.*) from solubility determinations in different organic solvents. This halide may therefore be considered, in analogy with titanium tetrachloride, to possess a tetrahedral structure with tin at the centre of grouping.

Application of Modified Formulae.—Kirkwood's equation (*loc. cit.*) has been considered to be the most reliable equation for representing the total molecular polarisation of a polar molecule when the mutual interaction between molecular dipoles is taken into account. The polarisation value given by this equation is thus considered to be the nearest to the true value, *i. e.*, the value which would be obtained by applying Debye's equation to the gaseous state. The molecular polarisation, determined

by Kirkwood's equation, must be higher than that determined by Debye's equation, as in the first case the molecule is considered to be acted upon by two fields of force: the external field and that arising from the surrounding dipoles. Consequently, it becomes easier for the molecule to be oriented, thus leading to an increase in the value of the orientation polarisation. In order to investigate the solvent effect, Kirkwood's as well as Henriquez' and Newton's equations (*loc. cit.*) were applied for calculating $P_{2\infty}$. The values obtained are shown in Table II from which it can be seen that $P_{2\infty}$ for one halide varies with the solvent, thus indicating that even those equations, which are based on a modified theory, do not satisfactorily account for the solvent effect. Similar conclusions were drawn by Smith and Witten (*loc. cit.*) with respect to some organic substances. The effect of the solvent on the ratio between $P_{2\infty}$ obtained from each modified formula and that obtained from Debye's formula, and the dependence of this ratio on the polarity of the substance have been traced. The data shown in Table III reveal that the ratio for one halide is nearly the same in the two different solvents and that the increase in polarity is accompained with a slight increase in the ratio. This result can be further supported when similar calculations are made on the Smith and Witten data. One can therefore predict that substances of near dipole moment values should be of the same ratio. However, further work is necessary to substantiate this prediction.

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SUBSTITUTION IN THE BENZOPYRONE SERIES. PART II*. SULPHONATION OF COUMARIN DERIVATIVES

By J. R. Merchant and R. C. Shah †

The sulphonation of coumarin, 6-nitrocoumarin, 7-hydroxy-4-methylcoumarin and its methyl ether, and 7-hydroxy-6-carboxy-4-methylcoumarin and its methyl ester with chlorosulphonic acid have been described. The structures of the sulphonated products have also been established.

During the work on the substitution reactions of benzopyrones, in this laboratory, the sulphonation of a number of coumarin derivatives has been investigated. From the literature (Suter, "The Organic Chemistry of Sulphur", Wiley, New York, p. 458) very little systematic work appears to have been done on the subject. The first attempt at sulphonation of coumarin was made by Perkin (*J. Chem. Soc.*, 1871, **24**, 49 ; 1875, **28**, 14) who obtained mono- and di-sulphonic acids which were later on shown by Sen and Chakravarti (this *Journal*, 1928, **5**, 433) to be the coumarin-6- and -6:8-disulphonic acids. The same authors also obtained the 8-sulphonic acid by the sulphonation of 6-nitrocoumarin. A few other coumarin derivatives were sulphonated (Krüger, *Ber.*, 1923, **56B**, 480), but the structure of the sulphonated products had not been established.

In the present investigation, chlorosulphonic acid was used as the sulphonating agent, when, in addition to the sulphonic acids, the sulphonyl chlorides were also obtained in some cases. The sulphonic acids were identified (vide Experimental). The sulphonyl chlorides could be easily hydrolysed with water to the corresponding sulphonic acids and were also obtained by heating the sodium sulphonates with excess of chlorosulphonic acid. This interconversion showed that the sulphonic acid and the sulphonyl chloride groups had entered the coumarin nucleus in the same positions. Sulphonamides or sulphanilides were prepared to characterise the sulphonyl chlorides.

Table I describes the experimental conditions under which the different coumarin derivatives were sulphonated.

Attempts to obtain known compounds from (I) or (III) by nitration, bromination, hydrolysis and alkali fusion were unsuccessful. Hence, the positions of the sulphonic acid groups in (I) and (III) were proved by oxidation of their sodium salts with permanganate in alkaline medium, as described by Sen and Chakravati (*loc. cit.*), when 5-sulphosalicylic acid was obtained in both the cases. No tri-substituted products could be obtained by the sulphonation of coumarin even under vigorous conditions of experiment.

The sulphonation of 6-nitrocoumarin occurred with difficulty, and even under drastic experimental conditions, only mono-sulphonated products, (V) and (VI), were obtained. The structure of (V) was proved by oxidising its sodium salt with alkaline permanganate, when 5-nitrosalicylic acid was obtained, showing that the sulphonation had taken place in the 3-position.

* Part I under publication.

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TABLE I

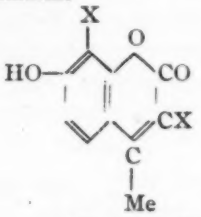
Substance.	Moles of chlorosulphonic acid.	Temp.	Period of heating.	Product of sulphonation.
Coumarin (C)*	2	100°	2 hrs.	(I) -6-sulphonic acid; (II) -6-sulphonyl chloride
	6	130-40°	3	(III) -3 : 6-disulphonic acid; (IV) -3 : 6-disulphonyl chloride
6-Nitro-C	10	,,	4	(V) -3-sulphonic acid; (VI) -3-sulphonyl chloride
7-Hydroxy-4-methyl-C	4	100°	2	(VII) -6-sulphonic acid; (VIII) -6-sulphonyl chloride
	4	130-40°	4	(IX) -6 : 8-disulphonic acid
	8	140°	4	(X) -3 : 6 : 8-trisulphonic acid
7-Hydroxy-3 : 6-dibromo-4-methyl-C	10	100°	2	(XI) -8-sulphonic acid
7-Hydroxy-3 : 8-dibromo-4-methyl-C	7·5	,,	2	(XII) -6-sulphonic acid; (XIII) -6-sulphonyl chloride
7-Methoxy-4-methyl-C	4·3	,,	2	(XIV) -6-sulphonic acid; (XV) -6-sulphonyl chloride
	8	60° (in dry $CHCl_3$)	3	(XVI) -3 : 6-disulphonic acid; (XVII) -3 : 6-disulphonyl chloride
7-Methoxy-3-bromo-4-methyl-C	4	100°	2	(XVIII) -6-sulphonic acid; (XIX) -6-sulphonyl chloride
7-Hydroxy-6-carbomethoxy-4-methyl-C	1	60° (in dry $CHCl_3$)	2	(XX) -7-hydroxy-6-carboxy-4-methylcoumarin-8-sulphonic acid + unchanged substance.
7-Hydroxy-6-carboxy-4-methyl-C	4	100°	2	(XXI) -3 : 8-disulphonic acid.

* 'C' stands for 'coumarin'.

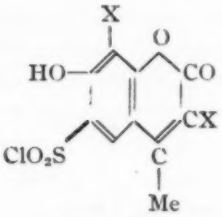
In order to prove the structure of (VII) the hydrolysis, nitration, alkali fusion, oxidation and methylation of its sodium salt were attempted, but no pure product could be isolated in any case. Demethylation of (XIV) to obtain (VII) was also unsuccessful. Bromination of the sodium salt of (VII) with even one mole of bromine in acetic acid medium at room temperature afforded 7-hydroxy-3 : 6 : 8-tribromo-4-methylcoumarin. A similar observation has been made by Dalvi and Sethna (this *Journal*, 1949, **26**, 359).

As (VIII) could be easily hydrolysed to yield (VII), attempts were made to establish the structure of (VIII). It has been observed (Suter, *loc. cit.*, p. 512) that sulphonyl chlorides, in general, are stable towards halogenation, and the same can be effected without modifying the sulphonyl chloride group. Hence, the bromination of (VIII) was carried out with 2 moles of bromine in acetic acid when a dibromosulphonyl chloride was obtained. Attempts were therefore made to prepare a dibromosulphonyl chloride by sulphonation of the two known dibromo derivatives of 7-hydroxy-4-methylcoumarin (Dalvi *et al.*, *loc. cit.*). 7-Hydroxy-3:6-dibromo-4-methylcoumarin, when heated with an excess of chlorosulphonic acid, did not furnish any sulphonyl chloride, but only the 8-sulphonic acid which on bromination yielded 7-hydroxy-3 : 6 : 8-tribromo-4-methylcoumarin, showing the position of the sulphonic acid group in (XI). Sulphonation of 7-hydroxy-3 : 8-dibromo-4-methylcoumarin, on the other hand, afforded a sulphonyl chloride (XIII) and a sulphonic acid which on bromination yielded

7-hydroxy-3 : 6 : 8-tribromo-4-methylcoumarin, thus indicating that the sulphonic acid group had entered the 6-position. The sulphonyl chloride (XIII) could be easily hydrolysed to (XII), identical with that obtained by the bromination of (VIII). Thus, (VII) and (VIII) are shown to be the 6-substituted products of 7-hydroxy-4-methylcoumarin.

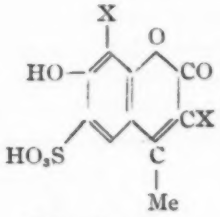


(X=H or Br)



(VIII : X = H)
(XIII : X = Br)

⇌



(VII : X = H)
(XII : X = Br)

Attempts to establish the constitution of the disulphonic acid (IX) by hydrolysis, oxidation, nitration, etc. proved fruitless. It was assigned the structure 7-hydroxy-4-methylcoumarin-6 : 8-disulphonic acid from analogy with other 7-hydroxycoumarins, wherein, if the 6-position was blocked, the 8-position was found to be attacked first in preference to 3-position. No definite proof could be obtained about the structure of the trisulphonic acid (X). It was, however, assigned the structure 7-hydroxy-4-methylcoumarin-3 : 6 : 8-trisulphonic acid. No di- or tri-sulphonyl chlorides of 7-hydroxy-4-methylcoumarin could be obtained even by heating the sodium salts of the di-(IX) and tri-(X) sulphonic acids with excess of chlorosulphonic acid.

The chlorosulphonylation of 7-methoxy-4-methylcoumarin first afforded the 6-sulphonyl chloride (XV) and the 6-sulphonic acid (XIV). The hydrolysis and nitration of the latter failed to furnish any definite products. The bromination of its sodium salt in acetic acid gave only 7-methoxy-3 : 6-dibromo-4-methylcoumarin. However, the structure of (XIV) was proved by the oxidation of its sodium salt with permanganate in alkaline medium, when 2-hydroxy-4-methoxy-5-sulphobenzoic acid was obtained. The position of the sulphonic acid group in the latter was proved by its bromination, when 2-hydroxy-4-methoxy-5-bromobenzoic acid (Rice, *J. Amer. Chem. Soc.*, 1926, **48**, 3129) was isolated, the constitution of which was confirmed by preparation of its methyl ester and by its decarboxylation to 4-bromoresorcinol-3-methyl ether. As a point of interest, β-resorcylic acid was sulphonated and the structure of the sulphonated product was proved to be 2 : 4-dihydroxy-5-sulphobenzoic acid.

The sulphonyl chloride (XV) on bromination afforded 7-methoxy-3-bromo-4-methylcoumarin-6-sulphonyl chloride, also synthesised by the chlorosulphonylation of 7-methoxy-3-bromo-4-methylcoumarin, when (XVIII) and (XIX) were obtained.

The disulphonated products (XVI) and (XVII) were proved to be the -3 : 6-disubstituted compounds of 7-methoxy-4-methylcoumarin. The structure of (XVI) was proved by brominating it when the known 7-methoxy-3 : 6-dibromo-4-methylcoumarin was obtained. The sulphonation of 7-methoxy-4-methylcoumarin with an excess of chlorosulphonic acid at 130°-140° furnished a trisulphonic acid which gave an intense violet coloration with alcoholic ferric chloride, showing that demethylation had occurred during sulphonation.

The sulphonation of 7-hydroxy-6-carbomethoxy-4-methylcoumarin with even one mole of chlorosulphonic acid at 60° was accompanied with the hydrolysis of the ester to the free carboxylic acid ; lower temperatures also did not effect any sulphonation. The ester, when sulphonated with 1 mole of chlorosulphonic acid in chloroform medium, gave a monosulphonic acid of 7-hydroxy-6-carboxy-4-methylcoumarin along with some unchanged material. To determine the position of the sulphonic acid group in the latter, its bromination was carried out in acetic acid medium, when 7-hydroxy-3 : 8-dibromo-6-carboxy-4-methylcoumarin was obtained. On the basis of the observations made by Dalvi and Sethna (*loc. cit.*) (XX) was assigned the structure 7-hydroxy-6-carboxy-4-methylcoumarin-8-sulphonic acid.

The sulphonation of 7-hydroxy-6-carboxy-4-methylcoumarin took place with difficulty and was found to be incomplete with 1 mole of chlorosulphonic acid at 100°, whereas at higher temperatures charring occurred. With an excess of chlorosulphonic acid, only a disulphonic acid (XXI) could be obtained. The structure of the latter was determined by bromination, when the known 7-hydroxy-6-carboxy-3 : 8-dibromo-4-methylcoumarin resulted (Dalvi and Sethna, *loc. cit.*).

The sulphonation of the methyl ethers of 7-hydroxy-6-carboxy-4-methylcoumarin and its methyl ester was always accompanied with demethylation.

In the sulphonation of 7-hydroxycoumarin derivatives, the 6-position has been found to be the most reactive, the 8- and 3- positions being next in order of reactivity. The reactivity of the 6- position has also been observed in the nitration of 7-hydroxy-4-methylcoumarin where although a mixture of 6- and 8- isomers is obtained, the 6-nitro derivative is found to be in a greater yield (Pechmann and Obermiller, *Ber.*, 1901, **34**, 666 ; Naik and Jadhav, this *Journal*, 1948, **25**, 171). The latter authors also obtained the 8-nitro derivative by the nitration of 7-hydroxy-6-carbomethoxy-4-methylcoumarin.

In the bromination of 7-hydroxycoumarin derivatives Dalvi and Sethna (*loc. cit.*) observed that the first bromine atom entered the 3-position. By brominating 7-hydroxy-4-methylcoumarin, they obtained a greater of 3 : 6- than 3 : 8-dibromo derivative, showing that the 6-position was more reactive than '8'.

In case of 7-methoxycoumarin derivatives, the 6-position is the most reactive, the 3-position being next in order of reactivity. Nitration of 7-methoxy-4-methylcoumarin also gives the 6-nitro derivative first. Bromination of the above coumarin also affords the -3 : 6-dibromo compound. It is interesting to note that no sulphonation occurs in the 8-position in 7-methoxycoumarins without demethylation taking place at the same time. Demethylation of this methoxy group has also been observed by Dalvi and Sethna (*loc. cit.*) during bromination of 7-methoxy-6-carbomethoxy-4-methylcoumarin.

EXPERIMENTAL

All melting points are corrected. Freshly distilled chlorosulphonic acid was used for sulphonation. The products of sulphonation, their m.p. etc. are listed in Table II.

TABLE II

Derivatives of sulphonic acids and sulphonyl chlorides.

Sulphonation product	M.P.	Barium salt/ Sulphonyl chloride	Analysis. Barium/Halogen. Found.	Calc.	*S*-Benzyl*iso*thiouronium derivative/ anilide or amide.	M.P.	% Nitrogen. Found.	Calc.
I	...	$C_{18}H_{10}O_{10}S_2Ba$	22.9	23.4	$C_{17}H_{16}O_3N_2S_2$	212-14°	7.2	7.1
II	119-20°	$C_9H_5O_4ClS$	14.2	14.5		186°	...	...
III	...	$C_9H_8O_6S_2Ba$	31.0	31.1	$C_{25}H_{26}O_8N_4S_4$	194-96°	8.9	8.8
IV	173-75°	$C_9H_4O_6Cl_2S_2$	20.4	20.7	$C_9H_8O_6N_2S_2$	>270°	9.2	9.2
					$C_{21}H_{18}O_8N_4S_2$	218-20°	6.2	6.1
V	...	$C_{18}H_8O_{14}N_2S_2Ba$	20.0	20.3	$C_{17}H_{15}O_7N_1S_2$	230-32°	9.9	9.6
VI	204-205°	$C_9H_4O_6NClS$	12.4	12.3	$C_9H_6O_8N_2S$	>290°	9.9	10.4
					$C_{15}H_{10}O_8N_2S$	130°	7.7	8.1
VII	...	$C_{20}H_{14}O_{12}S_2Ba$	21.2	21.2	$C_{15}H_{18}O_8N_2S_2$	180-82°	7.0	6.6
VIII	178-80°	$C_{16}H_7O_5ClS$	12.6	12.9	$C_{10}H_9O_5NS$	>290°	5.0	5.5
					$C_{16}H_{13}O_5NS$	245-47°	4.5	4.2
IX	...	$C_{10}H_6O_9S_2Ba$	29.6	29.2	...	...	...	...
X	...	$C_{20}H_{10}O_{24}S_6Ba_3$	32.7	33.3	...	...	...	...
XI	...	...	...	...	$C_{18}H_{16}O_6N_2Br_2S_2$	205-206°	4.5	4.8
XII	...	...	...	...	$C_{18}H_{16}O_6N_2Br_2S_2$	238° (decomp.)	5.1	4.8
XIII	210° (decomp.)	$C_{16}H_5O_5Br_2ClS$	7.6 (Sulphur analysis)	7.4	$C_{16}H_{11}O_5NBr_2S$	210-12°	2.8	2.9
XIV	...	$C_{25}H_{18}O_{12}S_2Ba$	20.1	20.3	$C_{19}H_{20}O_6N_2S_2$	250°	6.8	6.4
XV	203-204°	$C_{11}H_5O_5ClS$	12.4	12.3	$C_{11}H_{11}O_5NS$	>310°	5.0	5.2
					$C_{17}H_{15}O_5NS$	209-10°	4.1	4.1
XVI	...	$C_{11}H_8O_9S_2Ba$	27.9	28.3	$C_{27}H_{30}O_9N_4S_4$	244° (decomp.)	8.1	8.2
XVII	230-32°	$C_{11}H_8O_7Cl_2S_2$	18.5	18.35	$C_{23}H_{26}O_7N_2S_2$	245-47°	5.75	5.6
XVIII	...	...	...	...	$C_{19}H_{19}O_6N_2BrS_2$	280° (decomp.)	5.8	5.4
XIX	227-29°	$C_{11}H_8O_5ClBrS$	8.5 (Sulphur analysis)	8.7	$C_{17}H_{14}O_5NBrS$	236-38°	3.6	3.3
XX	...	$C_{22}H_{14}O_{16}S_2Ba$	18.3	18.7	$C_{19}H_{18}O_8N_2S_2$	209-11°	5.8	6.0
XXI	...	$C_{11}H_6O_{11}S_2Ba$	26.6	26.7	...	...	...	...

The free sulphonic acid (XIV) gave crystals of m.p. 175° (decomp.) from concentrated hydrochloric acid (Found: S, 11.85. $C_{11}H_{10}O_6S$ requires S, 11.5 %).

General Method for Sulphonation.—Chlorosulphonic acid was gradually added to the substance with cooling and the mixture, protected from moisture, was heated. After cooling, the contents were poured over crushed ice. The sulphonyl chlorides usually separated as pasty products which solidified on keeping. These were heated with ammonium carbonate or aniline to obtain the corresponding amides or anilides. The sulphonyl chlorides usually crystallised well from benzene or glacial acetic acid. The filtrate after removal of the sulphonyl chloride was saturated with sodium chloride, when the sodium salt of sulphonic acid separated in most cases. It was used as such for preparing the derivative with benzyl*iso*thiourea hydrochloride (prepared according to Chambers and Watts, *J. Org. Chem.*, 1941, **6**, 376). The derivatives were usually crystallised from dilute alcohol. The barium salt of the sulphonic acid was either prepared from the purified sodium salt by double decomposition with barium chloride, or from the orginal mother-liquor after complete removal of hydrogen chloride and neutralising the concentrate with barium carbonate. The barium salts were recrystallised from water, dried at 130°-140° and immediately analysed.

Oxidation of Coumarin-6-sulphonic and -3:6-disulphonic Acids.—The sodium salts of the sulphonic acids were oxidised with potassium permanganate in alkaline medium according to Sen and Chakravarti (*loc. cit.*). The potassium salt of the sulphonic acid

separating was used for the preparation of the derivative with benzyl*iso*thiourea hydrochloride. It was crystallised from dilute alcohol, m.p. 194-96°. (Found: N, 7.5. Calc. for $C_{15}H_{16}O_6N_2S_2$: N, 7.3%). Mixed m.p. with the derivative of 5-sulphosalicylic acid, prepared according to Meldrum and Shah (*J. Chem. Soc.*, 1923, **123**, 1988), showed no lowering.

The *oxidation of 6-nitrocoumarin-3-sulphonic acid* was carried out in the same way as described above. The product was free from sulphur and was crystallised from hot water in needles, m.p. 227-28°. Mixed m.p. with 5-nitrosalicylic acid (Meldrum and Hirwe, this *Journal*, 1928, **5**, 95) showed no lowering.

Bromination of 7-Hydroxy-4-methyl-6-sulphonic Acid (VII).—The sodium salt of the sulphonic acid (2 g.) was suspended in glacial acetic acid (8 c. c.) and a solution of bromine in acetic acid (10% ; 12 c.c., 1 *M*) was added to it with shaking. The mixture was kept at room temperature for five hours and filtered into water. The precipitate obtained was crystallised from acetic acid in white shining plates, m.p. 250-52°. (Found : Br, 57.8. Calc. for $C_{10}H_5O_5Br_3$: Br, 58.1%). Mixed m.p. with an authentic specimen of 7-hydroxy-3 : 6 : 8-tribromo-4-methylcoumarin (Dalvi and Sethna, *loc. cit.*) showed no lowering.

The same tribromo derivative was obtained by bromination of the sodium salts of 7-hydroxy-3 : 6-dibromo-4-methylcoumarin-8-sulphonic acid and 7-hydroxy-3 : 8-dibromo-4-methylcoumarin-6-sulphonic acid with an excess of bromine in acetic acid medium at 100°.

Bromination of 7-Hydroxy-4-methylcoumarin-6-sulphonyl Chloride (VIII).—The sulphonyl chloride (1 g.) was dissolved in glacial acetic acid (10 c.c.) by boiling and a solution of bromine in acetic acid (10% ; 11 c.c., 2*M*) was added gradually to the hot solution with shaking. After 6 hours at room temperature, the crystals of the bromo compound were filtered and recrystallised from acetic acid in white needles, m. p. 208-10° (decomp.). (Found : S, 7.6. Calc. for $C_{10}H_5O_5ClBr_2S$: S, 7.4%). Its mixed m.p. with the sulphonyl chloride obtained by the sulphonation of 7-hydroxy-3 : 8-dibromo-4-methylcoumarin showed no lowering.

Bromination of 7-Methoxy-4-methylcoumarin-6-sulphonic Acid (XIV).—The sodium salt (1 g.) was brominated with 2 moles of bromine in acetic acid medium. After heating on the water-bath for 15 minutes, the mixture was poured into water. The white precipitate obtained was crystallised from acetic acid in needles, m.p. 240°. Its mixed m. p. with 7-methoxy-3 : 6-dibromo-4-methylcoumarin (Dalvi and Sethna, *loc. cit.*) showed no lowering.

Bromination of 7-Methoxycoumarin-6-sulphonyl Chloride (XV).—The sulphonyl chloride was brominated as before with 2 moles of bromine in acetic acid. Crystallisation furnished white needles, m.p. 227-28°. (Found : S, 8.5. $C_{11}H_6O_5Cl\,BrS$ requires S, 8.7%).

Oxidation of 7-Methoxy-4-methylcoumarin-6-sodium sulphonate.—The substance (5 g.) was dissolved in 2*N*-KOH (75 c.c.) and a 4% solution of $KMnO_4$ (200 c.c.) was added dropwise with stirring. After heating on the water-bath for one hour, the mixture was filtered, acidified and concentrated to a small bulk. The product separating was used for the preparation of the barium salt and for the derivative with benzyl*iso*thiourea

hydrochloride, which crystallised from alcohol, m.p. 228-30° (decomp.). (Found : N, 7.1. $C_{16}H_{16}O_7N_2S_2$ requires N, 6.8%). (Found : Ba, 21.7. $C_{16}H_{14}O_{14}S_2Ba$ requires Ba, 21.8%). Mixed m.p. with the derivative of 2-hydroxy-4-methoxy-5-sulphobenzoic acid showed no depression.

The free sulphonic acid obtained by decomposition of the barium salt was crystallised from HCl (conc.) in green needles, m.p. 175-78° (decomp.). It was dried at 100° under vacuum and analysed. (Found : S, 13.5. Calc. for $C_8H_8O_7S$: S, 12.9%).

2-Hydroxy-4-methoxy-5 - sulphobenzoic Acid.—2 - Hydroxy-4-methoxybenzoic acid (5 g.) (prepared according to Gomberg and Johnson, *J. Amer. Chem. Soc.*, 1917, **39**, 1687) was heated with H_2SO_4 (conc., 25 g.) at 100° for 2 hours and then poured into brine when the sodium salt precipitated. It was used for preparing the derivative with benzyl*iso*thiourea hydrochloride, which crystallised from dilute alcohol, m.p. 230-32° (decomp.). Senhöfer and Brünner (*Chem. Zentrl.*, 1879, I, 566) sulphonated β-resorcylic acid and obtained a sulphonic acid to which they assigned the structure 2 : 4-dihydroxy-5 (?)-sulphobenzoic acid. The position of the sulphonic acid group in the latter was confirmed by its methylation to 2-hydroxy-4-methoxy-5-sulphobenzoic acid obtained above. The *S*-benzyl*iso*thiouronium derivative of 2 : 4-dihydroxy-5-sulphobenzoic acid was crystallised from dilute alcohol, m.p. 201-202°. (Found : N, 7.4. $C_{15}H_{16}O_7N_2S_2$ requires N, 7.0%).

Bromination of 2-Hydroxy-4-methoxy-5-sulphobenzoic Acid.—The sodium salt (2 g.) was brominated with a solution of bromine in acetic acid (10%, 12 c.c.). The mixture was heated on the water-bath for 10 minutes and poured into water. The precipitate obtained was crystallised from alcohol in white needles, m.p. 251-52°. (Found : Br, 32.5. Calc. for $C_8H_7O_4Br$: Br, 32.4%).

The same bromo compound was obtained by bromination of 2-hydroxy-4-methoxybenzoic acid. The structure of the bromo compound as 2-hydroxy-4-methoxy-5-bromobenzoic acid was confirmed by preparing its methyl ester, m.p. 143° (Rice, *loc. cit.*, records m.p. 143°) and by decarboxylating it to 4-bromoresorcinol-3-methyl ether, m.p. 83-84° (lit. m.p. 84°).

Bromination of 7-Methoxy-4-methylcoumarin-3 : 6-disodium disulphonate (XVI).—The bromination was carried out as usual with 3 moles of bromine in acetic acid. The product obtained after crystallisation from acetic acid had m.p. 240°. Its mixed m.p. with an authentic sample of 7-methoxy-3 : 6-dibromo-4 - methylcoumarin (Dalvi and Sethna, *loc. cit.*) showed no depression.

Bromination of 7-Hydroxy-6-carboxy-4-methylcoumarin-8-sodium sulphonate.—The substance (1 g.) was suspended in acetic acid (10 c.c.) and a solution of bromine in acetic acid (10% ; 6 c.c.) was added. The reaction mixture was boiled under reflux for 2 hours and poured into water. The product which had separated was crystallised from acetic acid in needles, m.p. 284-86° (decomp.). Its mixed m.p. with an authentic specimen of 7-hydroxy-6 - carboxy-3 : 8 dibromo-4-methylcoumarin (Dalvi and Sethna, *loc. cit.*) showed no lowering. The same dibromo compound was obtained by bromination of 7-hydroxy-6-carboxy-4- methylcoumarin-3 : 8-disodium disulphonate under identical conditions.

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SYNTHESIS OF NEW LOCAL ANAESTHETICS

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Piperidino- and diethylamino-acetyl-1-aminoanthraquinones, piperidino- and diethylamino-acetyl-2-aminofluorenes, and 3-amino-4-piperidino- and 3-amino-4-diethylamino-acetamidoanisols as well as their hydrochlorides have been synthesised, and their local anaesthetic activity tested.

Previous workers have proved that the essential structural requirements for a local anaesthetic are a lipolytic end containing an aromatic nucleus, a hydrophylic end consisting of a tertiary amino group, and an intermediate alkyl or substituted alkyl chain. Compounds having dialkylamino-alkylamino group connected to an aromatic or heterocyclic nucleus as the lipolytic moiety confer greater activity and less toxicity than the benzene analogues (Gupta, Shah and Gaind, this *Journal*, 1954, **31**, 845; Blicke and Parke, *J. Amer. Chem. Soc.*, 1939, **61**, 1200; Mattocks and Hutchinson, *ibid.*, 1948 **70**, 3474; Sargrevskaya and Neovadba, *J. Gen. Chem. U. S. S. R.*, 1938, **8**, 924).

Considering these facts, 1-aminoanthraquinone, 2-aminofluorene and 3-nitro-4-aminoanisol were taken as the starting primary amines which were condensed in the first stage with chloroacetyl chloride to obtain the corresponding chloroacetylamino compounds. These were further condensed with secondary amines, like piperidine and diethylamine. The nitro group present in 3-nitro-4-piperidinoacetamidoanisol and 3-nitro-4-diethylaminoacetamidoanisol was carefully reduced to amino group. The hydrochlorides of these bases have been prepared and their local anaesthetic activity tested.

The dihydrochlorides of 3-amino-4-piperidino- and 4-diethylamino acetamido-anisols have been found to be successful local anaesthetics. The hydrochlorides of piperidinoacetyl-1-aminoanthraquinone and diethylaminoacetyl-1-aminoanthraquinone produced only incomplete anaesthesia on rabbit's cornea. The 2-aminofluorene derivatives have been found to have a weak local anaesthetic action.

Experimental

Cholroacetyl-1-aminoanthraquinone.—Chloroacetyl chloride (3 c.c.), dissolved in pure benzene (12 c.c.), was gradually added to 1-aminoanthraquinone (5 g.), dissolved in benzene (30 c.c.). The reaction mixture was warmed at 70° on a water-bath for 1½ hours. Benzene was then distilled off and the residue washed with sodium bicarbonate solution and water and then dried. The product was recrystallised from alcohol in pale yellow crystals, m. p. 212°. (Found: N, 4.39; Cl, 11.79. $C_{16}H_{10}O_2NCl$ requires N, 4.67; Cl, 11.85%).

Piperidinoacetyl-1-aminoanthraquinone.—To chloroacetyl-1-aminoanthraquinone (5 g.), dissolved in absolute alcohol (50 c.c.), piperidine (5 c.c.) was added and the mixture refluxed for 4 to 5 hours. Alcohol and excess of piperidine were recovered by distillation and the residue washed with sodium bicarbonate solution and finally with water. The product was crystallised from 80% alcohol and recrystallised from benzene in bright yellow crystals, m. p. 235°. (Found: N, 7.84. $C_{21}H_{20}O_3N_2$ requires N, 8.04%).

The *hydrochloride* was prepared by dissolving the base (2 g.) in dry ether (20 c.c.) and saturating the solution with dry HCl gas. Ether was decanted off and the semi-solid mass was recrystallised from absolute alcohol, m. p. 320°. (Found: N, 7.14; Cl, 9.18. $C_{21}H_{21}O_3N_2Cl$ requires N, 7.28; Cl, 9.23%).

Diethylaminoacetyl-1-aminoanthraquinone.—It was likewise prepared and crystallised from benzene in glistening, brownish yellow plates, m. p. 164°. (Found: N, 8.12. $C_{20}H_{20}O_3N_2$ requires N, 8.33%).

The *hydrochloride* was crystallised from absolute alcohol, m. p. 256°. (Found: N, 7.42; Cl, 9.39. $C_{20}H_{21}O_3N_2Cl$ requires N, 7.51; Cl, 9.53%).

Chloroacetyl-2-aminofluorene.—To 2-aminofluorene (5 g.), dissolved in benzene (30 c.c.), chloroacetyl chloride (5 c.c), dissolved in the same solvent (20 c.c.), was gradually added with constant shaking, and warmed on a water-bath for 1½ hours at 65°. Benzene was then distilled off and the residue washed with sodium bicarbonate solution and water and then dried. The product was crystallised from alcohol, m. p. 172°. (Found: N, 5.39; Cl, 10.86. $C_{15}H_{12}ONCl$ requires N, 5.44; Cl, 10.95%).

Piperidinoacetyl-2-aminofluorene, prepared similarly as above, was crystallised from alcohol, m. p. 145°. (Found: N, 9.08. $C_{20}H_{22}ON_2$ requires N, 9.16%).

The *hydrochloride* was crystallised from absolute alcohol, m. p. 221°. (Found: N, 8.08; Cl, 10.27. $C_{20}H_{23}ON_2Cl$ requires N, 8.18; Cl, 10.36%).

Diethylaminoacetyl-2-aminofluorene was similarly prepared and crystallised from alcohol, m. p. 85°. (Found: N, 9.43. $C_{19}H_{22}ON_2$ requires N, 9.53%).

The *hydrochloride* was crystallised from absolute alcohol, m. p. 196°. (Found: N, 8.39; Cl, 10.71. $C_{19}H_{23}ON_2Cl$ requires N, 8.47; Cl, 10.74%).

3-Nitro-4-chloroacetamidoanisol.—3-Nitro-4-aminoanisol (2 g.) was dissolved in dry benzene (20 c.c.) and a solution of chloroacetyl chloride (1.4 c.c.) in dry benzene (15 c.c.) was added to it gradually during 10 minutes at 15°. The mixture was refluxed gently on a water-bath for 2 hours and then cooled. The greenish yellow precipitate after recovery of the solvent was washed several times with water, dried and crystallised from alcohol in greenish yellow plates, m. p. 101°. (Found: N, 11.36; Cl, 14.48. $C_9H_9O_4N_2Cl$ requires N, 11.45; Cl, 14.52%).

3-Nitro-4-piperidinoacetamidoanisol.—Piperidine (2 c.c.) was added to the above compound (2 g.), dissolved in absolute alcohol (30 c.c.). The mixture was refluxed gently on a water-bath for 5 hours. The alcohol was recovered and the semisolid mass was cooled, when yellow needles separated. The product was then washed several times with water, dried and crystallised from absolute alcohol, m. p. 130°. (Found: N, 14.26. $C_{14}H_{19}O_4N_3$ requires N, 14.33%).

3-Amino-4-piperidinoacetamidoanisol.—The preceding compound (2 g.), dissolved in 70% acetic acid (30 c.c.), was reduced with zinc dust (14 g.), added in small quantities at a time, keeping the mixture cooled in water so that the temperature did not rise above 40°. After addition of the whole of zinc dust, the mixture was gently heated on a water-bath at 60° for 3 to 4 hours, and filtered. The filtrate was cooled in ice and to this ammonium chloride (20 g.) was added. The solution was made

alkaline with ammonia and the base extracted with ether. The ethereal extract was dried over anhydrous sodium sulphate and the ether recovered. The product, thus obtained, was recrystallised from alcohol in brownish yellow plates, m. p. 122° .(Found : N, 15.86. $C_{14}H_{21}O_2N_3$ requires N, 15.97%).

The *dihydrochloride* was crystallised from absolute alcohol in brown plates, m. p. 212. (Found : N, 12.43 ; Cl, 21.01. $C_{14}H_{23}O_2N_3Cl_2$ requires N, 12.5 ; Cl, 21.13%).

3-Amino-4-diethylaminoacetamidoanisol was similarly prepared as above and obtained as reddish brown needles, m. p. 58°. (Found : N, 16.71. $C_{13}H_{21}O_2N_3$ requires N, 16.75%).

The *dihydrochloride* was crystallised from absolute alcohol in brown needles, m. p. 175°. (Found : N, 12.85 ; Cl, 21.82. $C_{13}H_{23}O_2N_3Cl_2$ requires N, 12.96 ; Cl, 21.92%).

The above hydrochlorides were tested for their local anaesthetic activity on rabbit's cornea. Each substance was used in 2% solution and compared with procaine hydrochloride solution of the same strength. The results are recorded in Table I.

TABLE I

Hydrochloride of :	Time for onset of anaesthesia (complete loss of reflex action).	Duration for which complete loss of reflex action lasted.
Piperidinoacetyl-1-aminoanthraquinone	Never complete (1.5 min.)	Incomplete anaesthesia for 31 min. (40 min.)
Diethylaminoacetyl- do	Incomplete (2 min.)	Incomplete for 32 min. (38 min.)
Piperidinoacetyl-2-aminofluorene	4 min. (1.25 min.)	22 min. (39 min.)
Diethylaminoacetyl- do	3.5 min (1 min.)	24 min. (40 min.)
* 3-Amino-4-piperidino-acetamidoanisol	2 min. (1.25 min.)	36 min. (39 min.)
3-Amino-4-diethylamino- do	1.5 min (1.5 min.)	41 min. (40 min.)

* refers to dihydrochlorides.

The value for standard substance are shown in parenthesis (here procaine hydrochloride was used as a standard substance).

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SUBSTITUTION IN THE BENZOPYRONE SERIES. PART III. SULPHONATION OF SOME 5-HYDROXYCOUMARIN DERIVATIVES

By J. R. Merchant and R. C. Shah

The sulphonation of 5-hydroxy-6-carboxy-4-methylcoumarin, its methyl ester, their methyl ethers, 5-hydroxy-4-methylcoumarin, its methyl ether and 5-hydroxy-4:7-dimethylcoumarin has been described. The structures of the sulphonated products have been proved wherever possible.

The present work describes the results obtained by the sulphonation of some hydroxycoumarin derivatives with chlorosulphonic acid (vide this *issue*, p. 35).

In general, it has been observed that the 5-hydroxycoumarins are sulphonated more readily than the 7-hydroxy ones (Table I). As before, the sulphonic acids were identified by the analyses of their barium salts and by their derivatives with benzyl*iso*thiourea hydrochloride. The sulphonyl chlorides were characterised by the preparation of anilides.

5-Hydroxy-6-carbomethoxy-4-methylcoumarin (prepared according to Sethna *et al.*, *J. Chem. Soc.*, 1938, 228) with a moderate excess of chlorosulphonic acid at 100° furnished the 8-sulphonic acid (I) and a sulphonyl chloride (II). The yield of the latter was maximum when sulphonation was carried out in dry chloroform medium. Also, it could be easily hydrolysed by boiling with water into the free sulphonic acid. The dry sodium salt of this acid, when heated with an excess of chlorosulphonic acid, gave the same sulphonyl chloride as (II). The latter as well as its anilide are insoluble in sodium carbonate, indicating that the ester group in the original coumarin is not hydrolysed during sulphonation. However, this hydrolysis was easily effected by heating the sodium salt of the sulphonic acid with alkali on a water-bath, when 5-hydroxy-6-carboxy-4-methylcoumarin-8-sulphonic acid was obtained. Attempts to prove the constitution of (I) by nitration or hydrolysis failed to provide definite products. The bromination of (I) was not carried out because the structures of the bromo derivatives of 5-hydroxycoumarins were not established at the time this work was carried out. The position of the sulphonic acid group in (I) was determined by the oxidation of its sodium salt with permanganate in alkaline medium, when a sulphonic acid of a phenol carboxylic acid was obtained. This indicates that the sulphonic acid group enters the 8-position in the coumarin. The analytical data of the oxidation product correspond to a dihydroxysulphobenzoic acid. It is found to be different from 2:4-dihydroxy-5-sulphobenzoic acid (cf. Part II, *loc. cit.*) and has therefore been assigned the structure 2:6-dihydroxy-3-sulphobenzoic acid.

The ester group in the original coumarin was hydrolysed when it was heated with a large excess of chlorosulphonic acid at 100°, affording the disulphonic acid (III) which was found to be identical with that obtained by the direct sulphonation of 5-hydroxy-6-carboxy-4-methylcoumarin. When the latter coumarin, its methyl ester or the sulphonic acids (I) and (III) were heated at 140° with an excess of chlorosulphonic

acid, trisulphonic acids, (IV) and (VI), were obtained which from the analysis of the barium salts appeared to be that of 5-hydroxy-4-methylcoumarin, decarboxylation and sulphonation occurring simultaneously.

Attempts to prepare a monosulphonic acid of 5-hydroxy-6-carboxy-4-methylcoumarin by direct sulphonation were unsuccessful, even under mild experimental conditions. However, by heating it with 2·5 moles of chlorosulphonic acid, the disulphonic acid (III) was obtained. With 10 moles of chlorosulphonic acid under the same conditions, the monosulphonyl chloride (V) also separated out in addition to the disulphonic acid (III). Attempts to establish the structure of (III) by nitration afforded 5-hydroxy-3 : 6 : 8-trinitrocoumarin which was also obtained by nitration of 5-hydroxy-6-carboxy-4-methylcoumarin and 5-hydroxy-4-methylcoumarin under identical conditions. However, oxidation of its sodium salt with alkaline permanganate furnished 2 : 6-dihydroxy-3-sulphobenzoic acid, showing that the sulphonic acid groups in (III) had entered the 3 : 8-positions.

The structure of the monosulphonyl chloride (V) has been proved by hydrolysing it with water when a free sulphonic acid, identical with that obtained by hydrolysis of 5-hydroxy-6-carbomethoxy-4-methylcoumarin-8-sulphonic acid (I), is obtained. Sulphonation of 5-methoxy-6-carboxy-4-methylcoumarin and its methyl ester was incomplete at 30°-40°, whereas at temperatures between 50° and 60° it was accompanied with demethylation, the products obtained being the same as that obtained with the corresponding hydroxycoumarins.

No monosulphonated products were formed on sulphonation of 5-hydroxy-4-methylcoumarin, but the disulphonic acid (VII) was easily obtained. Its structure was proved by its nitration in acetic acid medium when 5-hydroxy-6 : 8-dinitro-4-methylcoumarin was isolated, showing that the sulphonic acid groups in (VII) had entered the 6- and 8- positions. Attempts to prove the structure of the trisulphonic acid (VIII) failed to yield definite products. It was, however, assigned the structure 5-hydroxy-4-methylcoumarin 3 : 6 : 8-trisulphonic acid from the usual rules of substitution.

5-Methoxy-4-methylcoumarin on sulphonation in dry chloroform medium yielded a monosulphonic acid (IX). This acid did not give any coloration with alcoholic ferric chloride, indicating that no demethylation had occurred during sulphonation or if it had, the sulphonic acid group had entered the 3- or 8- position. Nitration of (IX) afforded a small amount of nitro compound free from sulphur (m. p. 140-45°). It could not, however, be sufficiently purified for purposes of analysis. No well-defined product could be obtained by the oxidation of (IX) with alkaline potassium permanganate. Hence, no definite structure could be assigned to (IX).

The sulphonation of 5-hydroxy-4 : 7-dimethylcoumarin did not take place so readily as in the case of 5-hydroxy-4-methylcoumarin. When heated with an excess of chlorosulphonic acid at 100°, a monosulphonic acid (X) and a monosulphonyl chloride (XI) were obtained. The latter was also obtained by heating the sodium salt of (X) with an excess of chlorosulphonic acid. This gave a violet coloration with alcoholic ferric chloride, showing that the sulphonic acid group in (X) had entered the 6-position. Nitration of (X) furnished a nitro compound, free from sulphur, which was assigned the structure 5-hydroxy-3 : 6 : 8-trinitro-4 : 7-dimethylcoumarin.

At 140°, with an excess of chlorosulphonic acid, 5-hydroxy-4 : 7-dimethylcoumarin yielded a sulphonic acid, different from (X) in that it did not form any derivative with benzyl*iso*thiourea hydrochloride. It developed a violet coloration with alcoholic ferric chloride and the analysis of its barium salt corresponded to a monosulphonic acid. The formation of the latter may probably be due to desulphonation of a higher sulphonic acid which might have been formed by sulphonation during concentration of the reaction mixture to obtain the barium salt.

From the sulphonation studies of 5-hydroxycoumarin derivatives, it appears that both the 6- and 8-positions are equally reactive. The sulphonation of 5-hydroxy-4-methylcoumarin furnishes only the 6 : 8-disulphonic acid, while that of 5-hydroxy-4 : 7-dimethylcoumarin yields the 6-sulphonated products.

In the nitration of 5-hydroxy-4-methylcoumarin, the first nitro group enters the 8-position. The nitration of 5-hydroxy-6-carboxy-4-methylcoumarin and its methyl ester also lead first to the formation 8-nitro derivatives (Parekh and Shah, this *Journal*, 1942, **19**, 335). On the other hand, the Fries migration of the acetate of 5-hydroxy-4-methylcoumarin (Sethna *et al.*, *loc. cit.*, p. 232) and of 5-acetoxy-4 : 7-dimethylcoumarin (Shah and Shah, *J. Chem. Soc.*, 1938, 1427) yields the 6-acetyl derivative in both cases.

Bromination of 5-hydroxy-4-methyl- and 5-hydroxy-4 : 7-dimethylcoumarins and their methyl ethers are found to yield first the 8-bromo derivatives in all cases (Lele, Parikh and Sethna, this *Journal*, 1953, **30**, 610). The second bromine atom has been found to enter the 6-position in case of the 5-hydroxycoumarins and the 3-positions in the case of methoxycoumarins.

The 5-methoxycoumarins were easily demethylated on sulphonation, and hence no definite idea could be obtained about the reactivity of the different positions.

Table I describes the different experimental conditions and products obtained on sulphonation of these coumarin derivatives.

TABLE I

Coumarin (C).	Moles of chlorosulphonic acid.	Temp.	Heated for	Product of sulphonation.
5-Hydroxy-6-carbomethoxy-4-methyl-C	2.5	100°	2 hrs.	(I)-8-sulphonic acid
				(II)-8 sulphonyl chloride
	15	,,	2	(III) 5-hydroxy-6-carboxy-4-methylcoumarin-3 :8-disulphonic acid.
	10	130°-140°	6	(IV) a trisulphonic acid
5-Hydroxy-6-carboxy-4-methyl-C	2.5	100°	2	(III)-3 :8-disulphonic acid
	10	,,	2	(III)-3 :8-disulphonic acid and (V) 8-sulphonyl chloride.
	10	140°	6	(VI) a trisulphonic acid.
5-Hydroxy-4-methyl-C	8	100°	2	(VII)-6 :8-disulphonic acid.
	8	140°	6	(VIII)-3 :6 :8-trisulphonic acid.
5-Methoxy-4-methyl-C	1	60° (dry $CHCl_3$)	1.5	(IX)-monosulphonic acid
5-Hydroxy-4 :7-dimethyl-C	Excess	100°	2	(X)-6-sulphonic acid and (XI)-6-sulphonyl chloride.

EXPERIMENTAL

All melting points are corrected. Freshly distilled chlorosulphonic acid was used. The products of sulphonation with their m.p. etc. are listed in Table II. The general method is the same as described in Part II (*loc. cit.*).

TABLE II

Derivative of sulphonic acids and sulphonyl chloride

Sulphonation products.	M. P.	Barium salt/ Sulphonyl chloride	Barium/ Halogen.		*S*-Benzyl*iso*-thiouronium derivative/ Anilide.	M. P.	% Nitrogen	
			Found.	Calc.			Found.	Calc.
I	–	$C_{34}H_{18}O_{16}S_2Ba$	17.3	18.0	$C_{29}H_{20}O_8N_2S_2$	222-24°	5.6	5.8
II	178-80°	$C_{17}H_9O_7ClS$	10.6	10.7	$C_{18}H_{15}O_7NS$	238-40°	3.3	3.6
III	—	$C_{11}H_6O_{11}S_2Ba$	26.1	26.7	$C_{27}H_{28}O_{11}N_4S_4$	209-10°	8.0	7.9
IV	–	$C_{16}H_{16}C_{24}S_8Ba_3$	33.0	33.3	...	...	...	...
V	218-20°	$C_{11}H_7O_7ClS$	11.1	11.1	$C_{17}H_{13}O_7NS$	260° (decomp.)	3.4	3.7
			(C=41.9; H=2.7)					
			(C=41.5; H=2.2)					
VI	–	$C_{20}H_{10}O_{24}S_6Ba_3$	33.3	33.3	...	...	...	...
VII	–	$C_{10}H_9O_9S_2Ba$	28.6	29.2	$C_{26}H_{28}O_4N_4S_4$	177-79°	8.1	8.4
VIII	–	$C_{20}H_{10}O_{21}S_6Ba_3$	33.0	33.3	...	...	...	...
IX	...	$C_{22}H_{18}O_{12}S_2Ba$	20.0	20.3	$C_{19}H_{20}O_8N_2S_2$	116-18°	6.0	6.4
X	...	$C_{22}H_{15}O_{12}S_2Ba$	19.9	20.3	$C_{19}H_{20}O_8N_2S_2$	182°	6.2	6.4
XI	164-66°	$C_{11}H_9O_5ClS$	12.4	12.3	$C_{17}H_{15}O_5NS$	201-203°	4.0	4.1

Hydrolysis of 5-Hydroxy-6-carbomethoxy-4-methylcoumarin-8-sodium sulphonate (I).—A solution of the substance (1 g.) in 10% NaOH solution (20 c.c.) was heated on a water-bath for 30 minutes, filtered and acidified, when a sodium salt separated. It was used for the preparation of the derivative with benzyl*iso*thiourea hydrochloride, crystallised from dilute alcohol, m.p. 198-200° (decomp.). (Found: N, 6.3. $C_{19}H_{18}O_8N_2S_2$ requires N, 6.0%). The mixed m.p. of this derivative with that of the sulphonic acid obtained by hydrolysis of 5-hydroxy-6-carboxy-4-methylcoumarin-8-sulphonyl chloride (V) showed no lowering.

Oxidation of 5-Hydroxy-6-carbomethoxy-4-methylcoumarin-8-sulphonic Acid (I).—To the sodium salt of the acid (3 g.), dissolved in 2*N*-KOH (40 c.c.), 4% solution of $KMnO_4$ (75 c.c.) was added dropwise, with ice cooling. The mixture was then heated on the water-bath for 1 hour, filtered, and the filtrate concentrated and acidified, when a substance separated. It contained sulphur and it did not melt. A part of it was used for preparation of the barium salt, which was crystallised from water and dried at 140° for analysis. (Found: Ba, 22.4. $C_{14}H_{10}O_{14}S_2Ba$ requires Ba, 22.8 %). The remaining part was used for preparation of the derivative with benzyl*iso*thiourea

hydrochloride. It was crystallised from dilute alcohol, m. p. 142-44°. It developed a violet coloration with EtOH-$FeCl_3$. (Found: N, 7.3. $C_{15}H_{16}O_7N_2S_2$ requires N, 7.0%). The same substance was obtained by the oxidation of 5-hydroxy-6-carboxy-4-methylcoumarin-3:8-disulphonic acid under identical conditions, and hence, it was assigned the structure 2:6-dihydroxy-3-sulphobenzoic acid.

Hydrolysis of 5-Hydroxy-6-carboxy-4-methylcoumarin-8-sulphonyl Chloride (V).—The substance (0.5 g.) was boiled with water till a clear solution was obtained and then saturated with brine when sodium salt of the sulphonic acid precipitated. The *S*-benzyl*iso*thiouronium derivative was crystallised from alcohol, m. p. 198-200°. The mixed m. p. with the derivative obtained from 5-hydroxy-6-carboxy-4-methylcoumarin-8-sulphonic acid, described above, showed no lowering.

Nitration of 5-Hydroxy-6-carboxy 4-methylcoumarin-3:8 disulphonic Acid.—The free disulphonic acid was obtained by decomposition of the barium salt. It crystallised from HCl (dil.) in white needles, m. p. 202-203°. The acid (0.6 g.) was suspended in glacial acetic acid (16 c.c.) and nitric acid (*d* 1.42, 5 c.c.) was slowly added. The mixture was heated on the water-bath for 30 minutes and poured over ice when a yellow precipitate was obtained. It crystallised from acetic acid in yellow needles, m. p. 208-209° (decomp.). (Found: N, 13.2. $C_{10}H_5O_9N_3$ requires N, 13.5%). The same nitro compound was obtained by the nitration of 5-hydroxy-6-carboxy-4-methylcoumarin and 5-hydroxy-4-methylcoumarin under identical conditions.

Oxidation of 5-Hydroxy-6-carboxy-4 methylcoumarin-3:8-disulphonic Acid.—The oxidation was carried out with alkaline permanganate, as described previously. The *S*-benzyl*iso*thiouronium derivative of the oxidation product had m. p. 142-44° and was found to be identical with that of 2:6-dihydroxy-3-sulphobenzoic acid, described before.

Preparation of 5-Methoxy-4-methylcoumarin-6-carboxylic Acid.—5-Methoxy-6-carbomethoxy-4-methylcoumarin (3 g.) (prepared according to Sethna *et al.*, *loc. cit.*) was shaken with 10% NaOH solution (75 c.c.) and heated on the water-bath for 30 minutes to a clear solution. Acidification gave a white precipitate which crystallised in needles, m. p. 216-18°. (Found: C, 61.4; H, 4.3. $C_{12}H_{10}O_5$ requires C, 61.5; H, 4.3%).

Nitration of 5-Hydroxy-4-methylcoumarin-6:8-disulphonic Acid (VI).—The free sulphonic acid, obtained by decomposition of the barium salt (0.5 g.), was dissolved in acetic acid (5 c.c.) and nitric acid (*d* 1.42, 2.0 c.c.) was added dropwise with cooling. The reaction mixture was kept overnight at room temperature and then poured over ice when a yellow precipitate was obtained which crystallised from methyl alcohol in yellow prisms, m. p. 182-84°. (Found: N, 10.2. $C_{10}H_6O_7N_2$ requires N, 10.5%). The mixed m. p. of the compound with 5-hydroxy-6:8-dinitro-4-methylcoumarin (prepared according to Parekh and Shah, *loc. cit.*, p. 338) showed no lowering.

Nitration of 5-Hydroxy-4:7-dimethylcoumarin-6 sulphonic Acid.—The free sulphonic acid was obtained as a precipitate during sulphonation of the coumarin on concentration of the filtrate after removal of the sulphonyl chloride. However, on trying to crystallise it, the sulphonic acid group was eliminated.

The crude sulphonic acid (0.5 g.) was suspended in glacial acetic acid (8 c.c.) and nitric acid (*d* 1.42, 4 c.c.) was added dropwise with cooling. The reaction mixture was left overnight at room temperature. On dilution with water, a yellow substance was obtained which crystallised from acetic acid in needles, m. p. 216-18° (decomp.). It did not contain any sulphur. (Found: N, 12.6. $C_{11}H_7O_9N_3$ requires N, 12.9%). It was assigned the structure 5-hydroxy-3 : 6 : 8-trinitro-4 : 7-dimethylcoumarin.

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ALTERNATING CURRENT ELECTROLYSIS. PART VI. ELECTROLYSIS OF SULPHURIC ACID SOLUTIONS WITH GOLD ELECTRODES

By K. M. Joshi

Effect of passing symmetrical alternating current in sulphuric acid solutions with gold electrodes has been invesitgated As observed previously, the current efficiency appears to decrease with frequency of alternation, concentration of electrolyte and progress of electrolysis. Higher current density favours the formation of electrode gas. Hydrogen peroxide is formed during electrolysis.

A theory has been advanced to explain the observed effects, based on recombination reactions taking place between the products liberated during consecutive half-cycles. Alternate oxidation and reduction of the electrode surface has been found to take place.

The results of experiments carried out with gold electrodes in sulphuric acid solutions in alternating current electrolysis are presented in this paper. The effects of frequency, current density, duration of electrolysis and concentration of electrolyte have been studied to elucidate the electrode reactions during A.C. electrolysis.

Marsh (*Proc. Roy. Soc.*, 1920, **97A**, 124) investigated the chemical effects of passing an A.C. of 40 cycles per second frequency between gold electrodes in dilute sulphuric acid, and found the rate of gas evolution to fall off with time and to increase with current density. He obtained definite evidence for the formation of an oxide during electrolysis. He suggested that alternate oxidation and reduction of the electrode surface might be taking place during A.C. electrolysis. Marsh, however, did not analyse the electrode gases obtained at the two electrodes.

Experimental

The experimental arrangement was the same as that used in previous investigations (this *Journal*, 1954, **31**, 278). The electrodes were made from bullion gold and measured 1 × 2 cm. These were fused into J-shaped glass tubing. The electrode gases were collected in gas collecting cups attached to gas burettes. The composition of electrode gas was determined by absorption in alkaline pyrogallol. The electrodes were cleaned with hot concentrated nitric acid and heated in a spirit lamp flame. These were then washed with water and rubbed with filter paper and immediately used. This procedure was found to furnish reproducible results.

During electrolysis it was observed that as soon as the current was switched on, provided that the current density was sufficiently high, gas evolution started at both the electrodes, but the rate of gas evolution fell off with time. The electrode at the end of the experiment was found to have been covered with a loosely adhering, orange-coloured deposit, insoluble in acids. Tests showed the deposit to be of elementary gold.

Effect of Frequency.—Table I records the effect of frequency on the current efficiency of gas evolution as well as on the composition of gas evolved at each electrode.

TABLE I

Electrolyte : $N/10$-H_2SO_4. Ampere hours passed = 0.4.

Frequency per sec.	Electrode I. Total gas.	H_2.	O_2.	Electrode II. Total gas.	H_2.	O_2.	% Current efficiency of gas evolution.
			Current = 600 ma.				
10	72.6 c.c.	50.4 c.c.	22.2 c.c.	68.8 c.c.	47.0 c.c.	21.8 c.c.	58.7
20	22.4	16.2	6.2	23.1	15.7	7.4	18.0
30	12.5	8.3	4.2	10.8	7.6	3.2	9.7
40	7.2	4.8	2.4	6.8	4.6	2.2	5.8
50	6.0	4.0	2.0	5.4	3.8	1.6	4.7
			Current = 200 ma.				
5	56.6	38.1	18.5	52.4	35.2	17.2	49.40
10	21.5	14.4	7.1	18.0	13.0	5.0	16.40
20	6.2	4.2	2.0	5.8	4.0	1.8	4.98
30	2.0	1.4	0.6	1.8	1.2	0.6	1.60
40	1.2	...	...	1.2	...	...	0.99
50	1.0	...	...	1.0	...	...	0.83

It can be seen from the data presented above that the current efficiency decreases with frequency of alternation. This has been a general observation in the case of A.C. electrolysis. If current efficiency were plotted against frequency of alternation, the curve would have the same shape as that obtained in earlier investigations. However, the results obtained in the present investigation on being compared with those obtained with platinum electrodes under identical conditions (Joshi, *loc. cit.*) show that the current efficiency with gold electrodes is greater. It will also be seen that the volume or composition of the gas evolved at the two electrodes is never the same.

Effect of Current Density.—Table II shows the effect of current density (C.D.) on the volume and composition of gas evolved.

TABLE II

Electrolyte : $N/10$-H_2SO_4.

C.D. (ma/cm^2).	Duration of exp.	Electrode I. Total gas.	H_2.	O_2.	Electrode II. Total gas.	H_2.	O_2.	% Current efficiency of gas evolution.
				Frequency = 20 per second.				
50	120 mins.	6.2 c.c.	4.2 c.c.	2.0 c.c.	5.8 c.c.	4.0 c.c.	1.8 c.c.	4.98
100	60	27.8	19.3	8.5	18.8	15.0	5.8	19.4
150	40	22.4	16.2	6.2	23.1	15.7	7.4	18.9
200	20	43.4	30.0	13.4	34.0	23.6	10.4	46.4
250	20	44.5	30.7	13.8	47.8	32.6	15.2	44.2
				Frequency = 40 per second.				
50	120	1.2	...	...	1.2	...	...	0.99
100	60	6.0	4.1	1.9	2.8	1.9	0.9	3.65
200	30	22.2	16.0	6.2	17.8	12.0	5.8	16.70
300	20	31.5	21.9	9.6	39.0	26.6	12.4	29.40

It will thus be seen that higher C.D. favours the formation of hydrogen and oxygen at the electrode. When the current efficiency is plotted against the current density, a linear curve at higher values of current density is obtained.

Effect of Electrolyte Concentration.—Table III records the effect of concentration of electrolyte on current efficiency.

TABLE III

Frequency = 10 per sec. Current = 600 ma. Time = 40 mins.

Electrolyte conc.	Electrode I.			Electrode II.			% Efficiency.
	Total gas.	H_2.	O_2.	Total gas.	H_2.	O_2.	
$N/20$	86.8 c.c.	60.0 c.c.	26.8 c.c.	81.3 c.c.	55.7 c.c.	25.6 c.c.	69.6 c.c.
$N/10$	72.6	50.4	22.2	68.8	47.0	21.8	58.7
$N/5$	24.7	17.0	6.8	21.2	14.7	6.5	19.1
N	10.6	7.4	3.2	9.8	6.8	3.0	8.5
$2N$	4.8	3.2	1.6	4.2	2.8	1.4	3.7

Effect of Time.—It was observed that with time the rate of gas evolution fell off. Table I shows the effect of time on the volume of gas collected at an electrode.

TABLE IV

Electrolyte: $N/10$-H_2SO_4. Current = 200 ma. Frequency = 20 per sec.

Electrode I.		Electrode II.	
Time.	Volume.	Time.	Volume.
3 mins.	1.1 c.c.	4 mins.	1.2 c.c.
6	1.95	7	2.2
10	2.8	11	3.0
14	3.6	16	3.8
20	4.6	21	4.8
28	5.8	29	5.8
42	7.3	43	7.4
60	9.2	60	8.6

It will thus be seen from the typical data presented above that the current efficiency of gas evolution decreases with the concentration of electrolyte as well as with the progress of electrolysis.

Formation of H_2O_2.—Qualitative tests indicate the presence of hydrogen peroxide in the electrolyte after a run of electrolysis as also the absence of persulphate in the electrolyte. Experiments were performed to find out a correlation between the amount of H_2O_2 formed and the composition of the electrode gas.

TABLE V

Electrolyte : $N/10$-H_2SO_4.

Frequency per sec.	Current.	Total H_2.	Total O_2.	H_2O_2 ($g. \times 10^{-3}$).	Available O_2 from H_2O_2.	Total O_2 liberated (sum of columns 4 and 6).	½ Volume of H_2 evolved.
			Ampere hours passed = 0.2				
5	400 ma	62.8 c.c.	26.5 c.c.	9.400	3.10 c.c.	29.40 c.c.	31 40 c.c.
20	600	15.9	6.8	3.096	1.02	7.82	7.95
10	500	50.0	24.2	2.185	0.72	24.92	25 00
10	300	27.5	13.7	0.015	0.05	13.75	13.75
10	200	13.9	5.8	3.035	1.00	6.80	6.95
			Ampere hours passed = 0.4.				
40	600	13 9	5.7	3.49	1.15	6.85	6.95
40	1000	34.0	15.2	4.86	1.60	16.80	17.00
30	400	7.2	3.0	1.71	0.60	3.60	3.60

It will be seen from the above table that if the total available oxygen from hydrogen peroxide formed in the electrolyte is added to the total oxygen evolved at both the electrodes, the total volume, thus computed, is equal to half the volume of hydrogen evolved. The agreement is within the experimental error though, where the volumes of gas collected are large the difference between columns 7 and 8 (above) is quite considerable.

DISCUSSION

The primary reactions which should take place in respect of consecutive anodic and cathodic discharge at a gold electrode are :

Anodic : $2\ OH^- \longrightarrow H_2O + O + e$ ... ... (1)

$O + O \longrightarrow O_2$ (surface reaction) ... ... (2)

$2\ Au + 3\ O \longrightarrow Au_2O_3$ ... ... (3)

Cathodic : $H^+ + e \longrightarrow H$ ... ... (4)

$H + H \longrightarrow$ (surface reaction) ... ... (5)

Consecutive anodic and cathodic discharge at the same electrode leads to recombination of discharged products. Thus :

$O..$ (metal) + $H..$ (metal) $\longrightarrow$ $OH..$ (metal) ... (6)

$2\ OH..$ (metal) $\longrightarrow H_2O + O..$ (metal) ... (7)

$Au_2O_3 + 6\ H \longrightarrow 2\ Au + 3\ H_2O$ ... ... (8)

The fact that current efficiency is low in A.C. electrolysis s[illegible] that a large proportion of discharge products is removed by the process of reversal [illegible] posite half-wave. Definite evidence has been obtained by the author with respect the formation and reduction of Au_2O_3 (to be communicated later). As frequency is increased, the duration of a half-cycle becomes smaller so that the products discharged at the

electrode have less chance to evolve as gas ; on the other hand, other processes, viz. reversal and ionisation of adsorbed gas, may predominate, leading to a lowering in current efficiency with frequency.

Higher current density will result in a greater amount of products being discharged in a unit time, leading to a greater concentration on the electrode surface. If the frequency of alternation i not very large, the discharged atoms during the half-cycle will combine and evolve as gas at a more rapid rate than at a lower current density. Moreover, a greater concentration during the cathodic cycle of hydrogen atoms will bring about a faster reduction of auric oxide formed during the previous half-cycle. Thus, the discharge of H^+ ions and the combination of hydrogen atoms discharged on the electrode will be facilitated. Also, during the anodic cycle, the rate of formation of the oxide and the evolution of oxygen will increase with current density. However, oscillographic work on the system, Au-H_2SO_4-Au, has shown that the area of electrode covered with the oxide does not increase linearly with current density. There seems to occur a saturation of the surface in respect of oxide formation, oxygen evolution taking place on the surface left bare. It is therefore easy to visualise that at a high current density, the coulombs contained in the half-cycle will not all be used for the formation of the oxide ; on the contrary, the coulombs available for the liberation of oxygen will be larger at a higher current density.

The formation of hydrogen peroxide probably takes place according to the same mechanism as that proposed in the case of platinum electrodes (Part III, *loc. cit.*). Thus :

$$H + O_2 \longrightarrow HO_2 \quad \ldots \quad \ldots \quad (9)$$

$$2\,HO_2 \longrightarrow H_2O_2 + O_2 \quad \ldots \quad \ldots \quad (10)$$

The conditions are favourable for the above reactions since consecutive half-cycles will leave H and O_2 on the surface of the electrode.

The lowering of current efficiency with progress of electrolysis can be explained on the basis of the picture presented above. With continued electrolysis, due to alternate oxidation and reduction of the electrode surface, the surface area of the electrode continually increases, thus lowering the effective current density. Thus the rate of gas evolution will decrease with the progress of electrolysis.

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THE BEHAVIOUR OF ELECTROLYTIES IN MIXED SOLUTIONS. PART I. VISCOSITY OF KCl IN DIOXAN-WATER MIXTURES AT 35°

By R. C. Acharya, P. K. Das and D. Patnaik

The viscosity of potassium chloride solution in dioxan-water mixtures at 10, 20, 30, 40 and 50% by weight of dioxan has been studied. Data obtained fit in excellently with a modified form of the Jones-Dole equation : $\eta/\eta_0 = 1 + A\sqrt{C} + BC^x$. '$B$' has been found to depend upon the composition of the solvent. It is suggested that the composition of the sphere of solvation is responsible for the magnitude of 'B'.

The aim of the present investigation has been to test the applicability of the Jones-Dole equation (*J. Amer. Chem. Soc.*, 1929, **51**, 2950) and in case of its non-applicability, to suggest a modified equation which would fit in with the experimental data. A satisfactory explanation has been advanced on theoretical grounds for 'A' by Falkenhagen and Vernon (*Phil. Mag.*, 1932, **14**, 537), but no such explanation has yet been offered for the constant 'B'. It is also the aim of the present study to explore the nature of 'B' by the use of mixed solvents. We have therefore studied the relative viscosity of solutions of potassium chloride in varying compositions of dioxan-water mixtures.

Experimental

Potassium chloride and dioxan used were of E. Merck's "extrapure" quality. Potassium chloride was recrystallised from triple distilled conductivity water, dried at 180° for 24 hours and stored in vacuum. Dioxan was left in contact with sodium wire for a week, then distilled and the middle fraction was used. At all stages of the experiment, rigorous precautions were taken to guard against evaporation of the non-aqueous component. To avoid evaporation, two limbs of the viscometer were attached to two flasks containing the same liquid. This arrangement was left undisturbed even when taking readings. All other experimental procedures were the same as recorded by Das (this *Journal*, 1954, **31**, 333) except that a further check of the vertical setting of the viscometer was done with a spirit level. The conductance readings were accurate to 2 in 1000. The working temperature was 35° ± 0.005°.

Table I

Solvent comp. = 50%. η/η_0.		Solv. comp = 40%. η/η_0.		Solv. comp. = 30%. η/η_0.		Solv comp. = 20%. η/η_0.		Solv comp. = 10%. η/η_0.	
*Conc.	Obs.	Calc.	Obs.	Calc.	Obs	Calc.	Obs.	Calc.	Obs.	Calc.
0.1000	1.0151	1.0155	1.0119	1.0125	1.0080	1.0084	1.0061	1.0062	1.0041	1.0040
0.0750	1.0120	1.0120	1.0093	1.0096	1.0071	1.0067	1.0049	1.0049	1.0032	1.0032
0.0500	1.0088	1.0084	1.0066	1.0068	1.0048	1.0049	1.0037	1.0036	1.0025	1.0024
0.0250	1.0045	1.0046	1.0039	1.0037	1.0029	1.0029	1.0021	1.0021	1.0016	1.0015
0.0100	1.0020	1.0022	1.0017	1.0018	1.0017	1.0014	1.0011	1.0013	1.0008	1.0008
0.0075	1.0011	1.0017	1.0014	1.0014	1.0014	1.0012	1.0010	1.0009	1.0007	1.0007
0.0050	1.0009	1.0013	1.0009	1.0011	1.0009	1.0009	1.0006	1.0007	1.0004	1.0006
0.0025	1.0006	1.0008	1.0006	1.0006	1.0006	1.0006	1.0003	1.0005	1.0002	1.0004
0.0010	1.0004	1.0004	1.0004	1.0004	1.0003	1.0003	1.0003	1.0001	1.0001	1.0002

†No. of grams of dioxan per 100 grams of the mixture.

*Conc. in g. moles/litre.

TABLE II

	Solv. comp. = 50%.		Solv. comp. = 40%.		Solv. comp. = 30%.		Solv. comp. = 20%.		Solv. comp. = 10%.	
Conc.	Λohm^{-1}.	$\Lambda_0$ohm^{-1}.	Λohm^{-1}.	$\Lambda_0$ohm^{-1}.	Λohm^{-1}.	$\Lambda_0$ohm^{-1}.	Λohm^{-1}.	$\Lambda_0$ohm^{-1}.	Λohm^{-1}.	$\Lambda_0$ohm^{-1}.
0.0100	60.1		75.7		99.4		111 4		139.4	
0.0075	60.7		76 8		100.8		112.5		139.8	
0.0050	61.7	66.0	78.0	83.25	101.6	108.5	113 8	120.0	140.3	142.2
0.0025	62.7		79.4		104.2		115 2		140 9	
0.0010	63.9		81.0		105.6		117.1		141.4	

TABLE III

Composition of the solvent.	$A \times 10^3$.	x.	$B \times 10^3$.
50%	9.22	1.00	12.6
40	7.82	1.00	10.0
30	6.93	0.92	5.25
20	6.84	0.99	3.98
10	6.64	1.02	2.00

DISCUSSION

The change in viscosity with concentration for aqueous solutions of electrolytes is represented satisfactorily by the Jones-Dole equation

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC \qquad \ldots \qquad \ldots \quad (1)$$

where η and η_0 are the viscosities of the solution and the solvent, C is the concentration, and A and B are constants. The value of 'A' can be calculated by using Falkenhagen and Vernons' equation (*loc. cit.*) with a knowledge of the mobility of the constitutent ions, the viscosity and the dielectric constant of the medium. In Table II the equivalent conductivities of potassium chloride solution at different composition of dioxan-water mixtures are shown and from these data, the equivalent conductivities at infinite dilution were obtained by plotting the equivalent conductivity against the square root of concentration and extrapolating the line to zero concentration. With the assumption that K^+ and Cl^- ions contribute equally towards the conductance at infinite dilution and using the data of Åkerlof and Short (*J. Amer. Chem. Soc.*, 1936, **58**, 1241) for dielectric constant of the medium, 'A' was calculated. The usual procedure to test the validity ot the Jones-Dole equation is first to see if a straight line is obtained by the plot of $\eta/(\eta_0 - 1)/\sqrt{C}$ against $\sqrt{C}$ and from the intercept of the straight line the value of 'A' can be obtained graphically. The satisfactory agreement between the calculated value of 'A' and that obtained by the graphical method is a further test of the Jones-Dole equation. The experimental data recorded in Table 1 do not satisfy the first test for the applicability of the Jones-Dole equation. The results are found to be satisfactorily represented if a slightly modified form of the Jones-Dole equation is employed :

$$\eta/\eta_0 = 1 + A\sqrt{C} + BC^x \quad \ldots \quad \ldots \quad (2)$$

In this equation 'A' remains unaltered in both form and implication. When x is one, the modified equation reduces to the original Jones-Dole equation. It is evident from equation (2) that the plot of log $\{\eta/\eta_0 - (1 + A\sqrt{C})\}$ against log C would give a straight line, and from the slope and the intercept, the values of x and 'B' could be calculated. The values of x, 'A' and 'B' for potassium chloride solution at different composition of dioxan-water mixtures are recorded in Table III.

To explain the nature of 'B', Cox and Wolfenden (*Proc. Roy. Soc.*, 1934, **145A**, 475) have attributed specific additive character to 'B', depending on the constituent ions. Since a single electrolyte, namely potassium chloride, has been used, the additive property attributed to 'B' is of not much avail. Asmus (*Z. Naturforsch.*, 1949 **4a**, 589) on the other hand suggests 'B' to be dependent on the lyotropic number and the entropy of hydrogen of the ionic species present in the medium. For aqueous solutions, Asmus' idea although relates the solvent to 'B', yet no direct proof has been advanced. A direct proof can be expected if 'B' changes with the change of composition of the solvent. This is only possible when a mixed solvent is used. The data recorded in Table III show that with the increase of the dioxan content in the solvent, the value of 'B' also increases, thus furnishing the proof that the magnitude of 'B' is dependent on the composition of the solvent.

We suggest that the sphere of solvation of the ions is responsible for the value of 'B'. In a single solvent, the solvation sphere is composed of only one type of molecule, and therefore it is the lyotropic number, as suggested by Asmus (*loc. cit.*), which determines the value of 'B'. In case of a mixed solvent, the solvation sphere will be composed of the molecules of the constituent components. Obviously, it is the nature and the number of molecules constituting the solvation sphere which would be responsible for 'B'. Hence, for a mixed solvent containing two types of molecules, it is to be expected that the value of 'B' would change with the change in composition of the mixture. The data recorded above fulfill this expectation.

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ON THE OXIDISING POWER OF BLUE CHROMIUM PEROXIDE IN RELATION TO ITS PROBABLE COMPOSITION

By Ram Chandra Rai

The oxidation values of the ethereal blue chromium peroxide (in two stages) and decomposition product have been investigated and the probable formula of the chromium peroxide is suggested.

In an earlier publication Rai and Prakash (*Proc. Ind. Acad. Sci.*, 1943, **18A**, 1) have studied the kinetics of the decomposition of the blue chromium peroxide in various organic media. They have further shown (*Z. anorg. Chem.*, 1954, **275**, 94) that the blue chromium peroxide on decomposition furnishes chromium^{3+}- dichromate, $Cr_2(Cr_2O_7)_3$. This substance, when strongly ignited, furnishes chromic oxide, Cr_2O_3. The theoretical ratio between Cr^{3+} - dichromate and chromic oxide is 1.23 and the ratios obtained lie between 1.22 and 1.26 for different preparations.

In the present communication the results on the oxidising power of the blue chromium peroxide in different stages are recorded so as to ascertain the probable composition of this blue peroxide.

Experimental

Preparation of the Blue Chromium Peroxide

The different samples of the blue peroxide were obtained from the following three sets of reacting mixtures.

First set: A 5% potassium dichromate solution (25 c.c.) was mixed with $2N$-H_2SO_4 (5 c.c.), and varying concentrations of H_2O_2 added; the blue peroxide in each case was extracted with 50 c.c. of ether.

Second set: A 4% chromic acid solution (25 c.c.) was mixed with varying concentrations of H_2O_2, and the blue peroxide in each case was extracted with 50 c.c. of ether.

Third set: Varying concentrations of chromic acid were mixed with 5 c.c. of $3N$-H_2O_2, and the blue peroxide in each case was extracted with 50 c.c. of ether.

These reactants were kept in ice, before they were mixed.

Estimation of Total Chromium.—The blue chromium peroxide was prepared by mixing the reactants, as outlined above, and the ethereal layer was separated in a separating funnel. A complete separation of the ethereal layer from the aqueous layer was carefully effected. The ethereal blue peroxide was taken in a Jena glass bottle and kept in ice; 10 c.c. of this solution was pipetted out in a tared silica crucible, evaporated on a water-bath, ignited and weighed as Cr_2O_3.

Oxidising Power.—The iodimetric titration was conducted in two stages:

First stage: The ethereal blue peroxide (5 c.c.) was added to a *neutral* aqueous solution of potassium iodide; the liberated iodine was titrated against a standard sodium thiosulphate ($N/9.65$) solution using starch solution as indicator. At this stage of the titration the colour of the solution was not green, but yellow.

Second stage: On completion of the first stage, to the same reaction mixture was added $2N$-H_2SO_4 (5 c.c.); the further quantity of iodine liberated was titrated against the same standard thiosulphate solution.

Oxidising Power of the Decomposed Product.—The blue ethereal peroxide (10 c.c.) was left in a 100 c.c. flask for the spontaneous slow decomposition, and when decomposed, the solution was made up to 100 c.c., 25 c.c. of which was pipetted out and added to KI solution, and acidified with H_2SO_4 (dil.). The liberated iodine was titrated against the same standard thiosulphate solution.

Oxidising Power of the Ethereal Layer after Decomposition of the Blue Peroxide.—The bottle containing the blue peroxide was left overnight; all the acid was decomposed and the ether was left. The latter (5 c.c.) was pipetted out in an acidified solution of potassium iodide and the liberated iodine was titrated against the same sodium thiosulphate solution. This liberation of iodine corresponded to the solubility of hydrogen peroxide in ether and was deducted from other readings, when the ratios of the various oxidation values were calcutated.

Thus from these titrations, the oxidising power of the blue peroxide in two stages and also of the decomposition product and the ether containing hydrogen peroxide, were determined, and from these results the various ratios, indicated in Tables I-III, were calculated.

TABLE I

First set mixture: 5% $K_2Cr_2O_7$ taken = 25 c.c. $2N$-H_2SO_4 taken = 5 c.c. Ether = 50 c.c.

1-5N-H_2O_2 used.	Cr_2O_3 present in 10 c.c. of blue peroxide.	Hypo used in titrating: 1st. stage.	2nd. stage.	10 c.c. of decomp. product.	10 c.c. of ether left.	Ratio $\frac{(c+d-f)}{b}$.	Ratio $\frac{(c+d-f)}{e}$.	Ratio d/e.	Ratio $\frac{(c-f)d}{d}$.
(a).	(b).	(c).	(d).	(e).	(f).	(g).	(h).	(i).	(j).
2 c.c.	0.0016 g.	2.0 c.c.	2.9 c.c.	2.2 c.c.	0.5 c.c.	2750	2.00	1.32	0.51
4	0.0038	1.9	2.9	2.2	0.3	1158	2.04	1.32	0.51
6	0.0104	5.9	9.3	7.0	0.7	1394	2.07	1.32	0.55
8	0.0142	7.2	11.6	8.8	0.5	1289	2.08	1.32	0.57
10	0.0216	12.8	18.4	14.35	0.6	1417	2.01	1.29	0.65
12	0.0292	15.8	23.4	18.30	0.6	1322	2.10	1.29	0.64
14	0.0178	9.4	14.4	10.75	0.6	1303	2.15	1.34	0.61
16	0.0312	18.2	28.2	21.25	0.5	1471	2.16	1.30	0.62
18	0.0496	26.7	44.1	34.10	0.5	1417	2.06	1.29	0.58

TABLE II

Second set mixture: 4% Chromic acid taken = 25 c.c. Ether taken = 50 c.c.

3N-H_2O_2 used.	Cr_2O_3 present in 10 c.c. of blue peroxide.	Hypo used in titrating: 1st. stage.	2nd. stage.	10 c.c. of decomp. product.	10 c.c. of ether left.	Ratio $\frac{(c+d-f)}{b}$.	Ratio $\frac{(c+d-f)}{e}$.	Ratio d/e.	Ratio $\frac{(c-f)}{d}$.
(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)
2 c.c.	0.0038 g.	1.8 c.c.	3.0 c.c.	2.2 c.c.	0.4 c.c.	1157	2.00	1.36	0.46
4	0.0072	3.9	6.4	4.9	0.4	1375	2.02	1.32	0.50
6	0.0088	5.6	8.8	6.7	0.6	1568	2.06	1.33	0.57
8	0.0100	6.1	9.8	7.4	0.4	1550	2.09	1.33	0.58
10	0.0171	10.1	15.8	12.1	0.6	1479	2.08	1.305	0.56
12	0.0255	16.0	24.2	18.2	0.5	1557	2.17	1.33	0.64
14	0.0232	14.2	22.5	17.25	0.6	1556	2.06	1.29	0.56
16	0.0402	23.2	37.2	27.3	0.6	1487	2.20	1.36	0.59

TABLE III

Third set mixture : $3N$-H_2O_2 taken = 5 c.c. Ether taken = 50 c.c.

4% Chromic acid used.	Cr_2O_3 present in 10 c.c. of the blue peroxide.	Hypo used in titrating 1st. stage.	2nd. stage.	10 c.c. of decomp. product.	10 c.c. of ether left.	Ratio $\frac{(c+d-f)}{d}$.	Ratio $\frac{(c+d-f)}{e}$.	Ratio d/e.	Ratio $\frac{(e-f)}{d}$.
(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)
2 c.c.	0.0032 g.	1.5 c.c.	2.3 c.c.	1.5 c.c.	0.4 c.c.	1062	2.20	1 50	0.48
5	0 0056	2.2	3.4	2.3	0.7	875	2.10	1.48	0.45
10	0.0178	6.2	10.1	7.6	0.7	876	2.03	1.33	0.54
15	0 0178	6.1	10.0	7.65	0.6	872	2.04	1.30	0.55
20	0.0258	9.1	14 4	10.9	0.6	886	2.09	1.32	0.59
25	0.0260	9.3	14.7	11.3	0.4	908	2.09	1.30	0.60
30	0.0170	6.0	9.1	7.0	0.4	864	2.07	1.30	0.59
40	0 0128	5.0	8.2	6.15	0.4	1000	2.08	1.33	0.53
50	0.0176	5.7	9.0	7.1	0.4	812	2.01	1.26	0.58

DISCUSSION

The following observations are made from the results recorded in Tables I, II and III.

(*i*) The amount of available oxygen from different samples of the blue peroxide is very nearly proportional to the amount of Cr^{3+}-oxide (Cr_2O_3) content. The ratios shown in the column (g) lie between 1.3 and 1.5×10^3 (Tables I and II) ; the values are, however, lower in Table III, ranging from 850 to 1000. The fluctuations are either due to the variations in the distribution of hydrogen peroxide in aqueous and ether layers or to the fact that the blue peroxide is not always of a definite composition.

(*ii*) The ratio between the total oxidising power of the blue peroxide and the oxidising value of the decomposition product obtained from the same quantity of the blue peroxide is very nearly 2 : 1 (column h). We have shown in the previous publication (*loc. cit.*) that this "decomposition product" has the composition of chromium dichromate, $Cr_2(Cr_2O_7)_3$. This ratio is significant in deciding the composition of the blue peroxide.

(*iii*) The ratio between the oxidation value of the second stage titration of the blue peroxide and the "decomposition product" obtained from the same volume of the blue peroxide is near about 1.33, as seen from the column (i) of the three tables.

(*iv*) The ratio between the oxidation values in the "first" and 'second" stage titrations lies between 0.5 and 0.6, as seen from the column (j) of the three tables.

Schwarz and Giess and their collaborators (*Ber.*, 1932, **65**, 871 ; 1933, **66B**, 330 ; Schwarz and Elstner, *Ber.*, 1936, **69**, 575 ; see also Rosenheim, Hakki and Krause, *Z.*

anorg. Chem., 1932, **209**, 175) have ascribed the formula CrO_5 to the blue peroxide. Our view is that the peroxide is of an indefinite composition, which only as its higher limits may show this composition. Ordinarily it corresponds to the composition $CrO_{3.75}$ or Cr_8O_{30}. Since on its spontaneous decomposition it furnishes chromium dichromate, during its reactivity it shows the following equilibrium :

$$Cr_8O_{30} \rightleftharpoons Cr_2(Cr_2O_{10})_3 \rightleftharpoons Cr_2[(CrO_5)_2]_3$$

This for convenience, we may term chromium perchromate.

In the "first stage" of the iodimetric titrations (in absence of acids) the decomposition proceeds to

$$Cr_8O_{30} \rightarrow Cr_8O_{24} + 6O \quad \ldots \quad \ldots \quad (i)$$

In the "second stage" of iodimetric titration, the decomposition proceeds to the final chromium oxide :

$$Cr_8O_{24} \rightarrow 4Cr_2O_3 + 12\,O \quad \ldots \quad \ldots \quad (ii)$$

We have already stated that on the spontaneous decomposition of the blue peroxide, chromium dichromate is obtained which is a water-soluble substance and which has the oxidation power similar to other dichromates :

$$Cr_2(Cr_2O_7)_3 \rightarrow 4Cr_2O_3 + 9\,O \quad \ldots \quad \ldots \quad (iii)$$

The ratio of the available oxygen from equations (*i*) and (*ii*) is 1 : 2, as shown in column (j) ; the ratio of the available oxygen from equations (*ii*) and (*iii*) is 12 : 9 or 1 : 1.33, as shown in column (*i*). The ratio between the total oxygen from equations (*i*) and (*ii*), taken together, and the equation (*iii*) is 18 : 9 or 2 : 1, as shown in column (h).

If the blue chromium peroxide be regarded to have at some stage the composition of chromium 'perchromate', $Cr_2(Cr_2O_{10})_3$, the decomposition product "chromium dichromate" is attained through the following stages :

$$Cr_2(Cr_2O_{10})_3 \longrightarrow Cr_2(Cr_2O_8)_3 \rightarrow Cr_2(Cr_2O_7)_3.$$

In case the blue peroxide is assumed to be of the composition CrO_5, as proposed by other workers, the various stages of the decomposition would be as follows :

$$\underset{\text{(Blue peroxide).}}{8\,CrO_5} \xrightarrow{-19\,O} \underset{(Cr^{3+}-\text{dichromate}).}{Cr_8O_{21}} \xrightarrow{-9\,O} \underset{(Cr^{3+}\text{-oxide}).}{4\,Cr_2O_3}$$

This mechanism would demand the ratio between the total available oxygen and the oxygen available from chromium dichromate to be 28 : 9, *i.e.*, 3.1 : 1 ; whereas our ratios in column (h) indicate it to be near about 2 : 1. This leads to the view that the blue chromium peroxide has a composition something like $CrO_{3.75}$ or rather Cr_8O_{30}, and not CrO_5.

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AN ANALYSIS OF THE NEUTRALISATION CURVES OF THE COLLOIDAL ACIDS. PART II

By S. L. Gupta

The potentiometric and conductometric titration curves of some colloidal clay acids have been theoretically analysed. The analysis shows that the experimental curves for the two clay sols reflect a combination of two effects, viz., neutralisation of a polybasic acid in true solution and ion adsorption.

In a previous communication (Gupta, this *Journal*, 1956, **33**, 587), a model was proposed to explain the neutralisation curves of acid colloidal ion exchangers, and certain mathematical formulations were made on the basis of the model which were shown to fit satisfactorily with the experimental data of a silicic acid sol. The present paper seeks to explain some clay-acid titrations on the basis of the same model and assuming the same mathematical expressions derived there.

It has been shown (Part I) that the total acidity of the colloid can be divided into two parts, C_a and C_t, where C_a determines the amount of H^+ ions present in the micellar solution in a form available for exchange by other cations, the exchanged H^+ ions being subsequently neutralised by the OH^- ions of the added base present in the intermicellar solution, and C_t represents a polybasic acid forming the outer surface of the colloidal particles capable of direct neutralisation by the OH^- ions, the corresponding cations of the added base being present in the intermicellar solution. The cations replacing the H^+ ions in the micellar solution are supposed to be bound or adsorbed and do not record their activities on a corresponding reversible electrode. It has also been shown that the initial slope of the neutralisation curve of the colloidal polybasic acid, in which the active groups are distributed on a large surface, can be represented by a monobasic acid C_1 with a dissociation constant k_1, where C_1 constitutes a fraction of the total intermicellar acidity, C_t. As the titration proceeds beyond C_1, the value of the active monobasic acidity has to be increased to C_2 with a lower order dissociation constant, k_2, to explain the next stretch, and so on. In this way the whole neutralisation curve may be approached when the last stretch of the curve may be represented by a monobasic acid, C_n, with a dissociation constant k_n, where $C_n = C_t$. The expression derived for the initial stretch, when a mono-acidic base like NaOH has been used for titration, is

$$b = C_a + \frac{C_1 k_1}{k_1 + x} + \frac{K_w}{x} - \frac{x.\,C_a}{\frac{C_1 k_1}{k_1 + x} + \frac{K_w}{x}} - x \qquad \ldots \quad (1)$$

where $x = (a_{H^+})_t$, *i.e.* the free or the intermicellar H^+ ion activity and K_w is the ionic product of water. For the second stretch the equation takes the form

$$b = C_a + \frac{C_2 k_2}{k_2 + x} + \frac{K_w}{x} - x \qquad \ldots \qquad \ldots \quad (2)$$

and for subsequent stretches (C_3, k_3), (C_4, k_4) etc. replace (C_2, k_2) in the above equation.

The necessary experimental data presented here for the purpose of evaluation and comparison have been obtained from the works of Mitra (*Indian J. Agric. Sci.*, 1936, **6**, 555). The abscissas in the curves have been recalculated in terms of normality of the added base and shown as such in the figures to facilitate comparison between the calculated and the experimental values.

In applying the above formulations, the initial p_H has been calculated from the slope of the curve and a slight parallel elevation of the evaluated curve has been observed in many cases (cf. Part I, *loc.cit.*), the coincidence in some cases being accidental as in the following titration of a clay sol.

Sol C_1.—This sol was isolated from Ganges silt by electrodialysis of the clay fraction which was previously treated with 6% H_2O_2 and leached with 0.05 *N*-HCl. The resulting sol contained 0.72 g. of the colloid per litre and had an average p_H of 5.05. Its ultrafiltrate analysis showed no trace of Cl^- ion so that free hydrochloric acid was absent. The acid at inflexion was read at 1.91×10^{-5} *N* for titration with NaOH and 5.7×10^{-5} *N* with $Ba(OH)_2$. The curves are shown in Fig. 1.

The equation (1) has been found to apply up to range PQ, and for subsequent stretches, *i.e.* QR, RS and ST, equation (2) has been applied with necessary *C* and *k* values evaluated from the slope. The initial H^+ ion concentration and the value of C_a (which is somewhat less than the inflexion point value) have been found to be 7.08×10^{-6} *N* corresponding to p_H 5.15 and 1.7×10^{-5} *N* respectively. Table I records the results of analysis, and the '*b*' values, marked with asterisks, were taken for computing the curve shown in full line, which is also the experimental curve.

FIG. 1

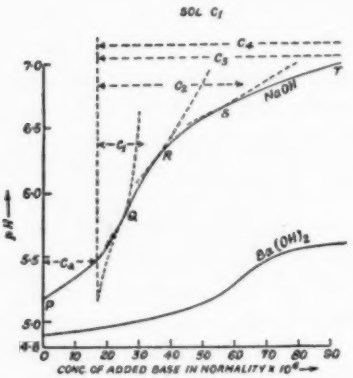


TABLE I

$C_1 = 14.158 \times 10^{-6}$ *N*. $k_1 = 7.079 \times 10^{-6}$.

p_H	5.15	5.25	5.50	5.75	6.00	6.50
$b \times 10^6$	0.00*	4.03*	18.14*	23.87*	27.04	29.85

$C_2 = 45.36 \times 10^{-6}$ *N*. $k_2 = 3.893 \times 10^{-7}$.

p_H	5.75	6.00	6.25	6.50	6.75
$b \times 10^6$	23.37	28.72*	35.06*	41.71	46.91

$C_3 = 128.1 \times 10^{-6}$ *N*. $k_3 = 9.526 \times 10^{-8}$.

p_H	6.00	6.25	6.50	6.75	7.00
$b \times 10^6$	27.14	35.00*	46.35*	61.15	79.42

$C_4 = 356.3 \times 10^{-6}$ *N*. $k_4 = 2.715 \times 10^{-8}$.

p_H	6.50	6.75	7.00	7.25
$b \times 10^6$	44.87	64.04*	93.00*	115.6

As has been shown earlier (Part I, *loc. cit.*), the evaluated dissociation constants are only averages, acting over a particular range, and do not represent any true constancy, because the fundamental assumption involved is that as the active intermicellar acidity increases, the dissociation constant drifts slowly to lower and lower values due to polybasicity of the colloid. The clay acid is fundamentally a weak acid having the dissociable groups – SiOH or – AlOH and the flat run approximately up to the inflexion point is a measure of the micellar or adsorbable H^+ ions, *i. e.* C_a, and does not signify any strong acid character.

The equation (1) cannot be applied to titrations with bivalent bases because the Donnan equilibrium involved in its deduction has to be modified accordingly. As the Donnan equilibrium is not significantly involved after the inflexion point, it is expected that the NaOH and $Ba(OH)_2$ curves should be identical or, say, parallel in this region where we are concerned with neutralisation as in true solution, and equation (2) holds good. The $Ba(OH)_2$ curve in Fig. 1, however, shows a greater extent of flat run than that due to NaOH and a continued flat portion after the inflexion point. This can be explained by the fact that the Ba^{2+} ions induce aggregation and thus increase the value of C_a, diminishing the value of C_f by a corresponding amount. A reference to the model in Part I (*loc.cit.*) will show that aggregation helps in the conversion of some of the intermicellar groups into micellar groups and the opposite effect takes place when an aggregate breaks up. Consequently, a greater amount of acidity at inflexion and a corresponding flat run were obtained by using a bivalent base like $Ba(OH)_2$. A slow process of continued aggregation with simultaneous removal of Ba^{2+} ions from the intermicellar solution will also account for the continued flattening even after the inflexion point which marks the saturation of the existing micellar groups.

Sol C.—This sol was also obtained from Ganges silt in the same way as sol C_1, but in its isolation the hydrochloric acid pretreatment was omitted. Its colloid content was found to be 0.44 g. per litre and, peculiarly enough, its ultrafiltrate analysis showed the presence of free hydrochloric acid in a strength of 9.5×10^{-5} N in the sol. As in the case of silicic acid sol, previously analysed (Part I, *loc. cit.*), we have to use here the corrected equations:

$$b = C_a + \frac{C_1 k_1}{k_1 + x} + \frac{K_w}{x} + r - \frac{x.C_a}{\frac{C_1 k_1}{k_1 + x} + \frac{K_w}{x} + r} - x \quad \ldots \quad (3)$$

for the initial stretch, where $r = (a_{Cl^-})_i$, and

$$b = C_a + r + \frac{K_w}{x} + \frac{C_2 k_2}{k_2 + x} - x \quad \ldots \quad (4)$$

etc. for the subsequent stretches. The value of $(C_a + r)$ has been evaluated at 24.5×10^{-5} N from the curve shown in Fig. 2 (which is necessarily slightly less than the inflexion point value, 28.0×10^{-5} N, reported in the text) and since $r = 9.5 \times 10^{-5}$ N, one gets $C_a = 15 \times 10^{-5}$ N. The other evaluated constants and the results of analysis are shown in Table II.

TABLE II

$C_1 = 9.272 \times 10^{-5} N$. $k_1 = 8.654 \times 10^{-5}$.

p_H	4.0	4.5	5.0	5.5	6.0
$b \times 10^5$	0.0	19.20*	26.72*	30.68*	32.63
$(a_{H^+})_t \times 10^5$	10.0	3.162	1.0	0.3162	0.100
$(a_{Na^+})_t \times 10^5$	0 0	8.33	12.80	15.97	17.71
$\kappa \times 10^5$	5.01	2.69	2.11	2.03	

$C_2 = 15.62 \times 10^{-5} N$. $k_2 = 1.572 \times 10^{-6}$.

p_H	5.5	5.825	6.5	7.0
$b \times 10^5$	29.37	32.35*	37.2*	39.1
$(a_{H^+})_t \times 10^5$	0.3162	0.1496	0.03162	0.01
$(a_{Na^+})_t \times 10^5$	14.37	17.35	22.2	24 1
$\kappa \times 10^5$		2.053	2.317	

$C_3 = 23.72 \times 10^{-5} N$. $k_3 = 3.442 \times 10^{-7}$.

p_H	6.5	7.0	7.5	8.0
$b \times 10^5$	36.85	42.88*	46.27*	47.55
$(a_{H^+})_t \times 10^5$	0.03162	0.01	0.00316	0.001
$(a_{Na^+})_t \times 10^5$	21.84	27.88	31.27	32.55
$\kappa \times 10^5$		2.667	2.88	

The 'b' values, marked with asterisks, show the full line theoretical curve in Fig. 2. The $(a_{Na^+})_t$ has also been evaluated from the electroneutrality relation,

$$(a_{Na^+})_t = (a_{R^-})_t + (a_{OH^-})_t + (a_{Cl^-})_t - (a_{H^+})_t$$
$$= \frac{C_1 k_1}{k_1 + x} + \frac{K_w}{x} + r - x \qquad \ldots (5)$$

for the initial stretch and replacing (C_1, k_1) in the above equation by (C_2, k_2) etc. for other stretches, and has been incorporated in the above table. The amount of Na^+ ion adsorbed at any p_H can also be computed, if neceassary, from the relation $(a_{Na^+})_a = b - (a_{Na^+})_t$. The values for the specific conductivity (κ), shown in Table II, have been obtained from the relation

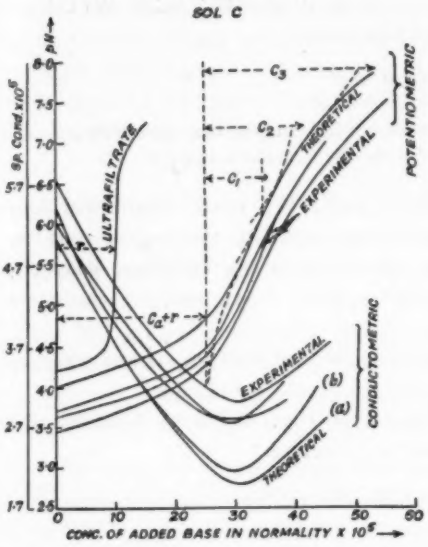
$$\kappa = \frac{U_{H^+}(a_{H^+})_t + U_{Na^+}(a_{Na^+})_t + V_{Cl^-}(a_{Cl^-})_t}{1000} \text{ mhos},$$

neglecting the contributions due to OH^- ion in acid solution and the mobility of the sluggish colloid anions. The adsorbed H^+ and Na^+ ions being part of the micelle are supposed not to take part in the conduction of the current. The following limiting equivalent conductivities at 35° have been assumed for the different ionic species:

$$U_{H^+} = 404,\ U_{Na^+} = 64 \text{ and } V_{Cl^-} = 93, \text{ ohms}^{-1}\ \text{cm}^{-1}.$$

It will be seen from curve (a), Fig. 2, that the calculated conductivity curve from the evaluated potentiometric data has almost the same slope and shows the same rounded minimum as has been obtained experimentally, only the calculated curve is situated somewhat lower. This is not surprising as the fact, that a discrepancy between the absolute values of ionic concentrations obtained from potentiometric and conductometric data occurs in these systems, is already well known, though the reason is still somewhat obscure. Also, the inherent difficulty in obtaining identical curves in these system by different measurements for the same titration has been emphasised by the parallel sets of potentiometric and conductometric experimental curves. These curves were obtained (Mitra, *loc. cit.*) by using a titration cell suitable for simultaneous conductometric and potentiometric measurements in conjunction with accessory instruments suitable for accurate work.

FIG. 2



If we do not wish to neglect the mobility of the clay ions, then neglecting the small OH^- ion concentration, the formula for the specific conductivity κ becomes

$$\kappa = \frac{U_{H^+}(a_{H^+})_f + U_{Na^+}(a_{Na^+})_f + V_{Cl^-}(a_{Cl^-})_f + V_{R^-}(a_{H^+} + a_{Na^+} - a_{Cl^-})_f}{1000} \text{ mhos},$$

where V_{R^-} represents the limiting equivalent conductivity of the clay particles for the ionised spots. Curve (b) in Fig. 2 shows the conductometric curve for this change accepting a small arbitrary value of 20 $ohms^{-1}$ cm^{-1} (Mukherjee *et al.*, *Indian J. Agric. Sci.*, 1936, **6**, 517, 531) for the equivalent conductivity per equivalent of charge on the clay particles (cf. Gupta, *Science & Culture*, 1956, **21**, 749 ; **22**, 282 ; 1957, **22**, 401).

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The abscissa for sol H/20 in Fig. 6 in Part I (this *Journal*, 1956, **33**, 587) should *read* 0, 5, 10, 15 and 20 *for* 0, 20, 40, 60, and 80.

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A STUDY OF COMPLEXES OF BLUE PEROXYCHROMIC ACID WITH PYRIDINE AND PIPERIDINE

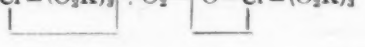
By Ram Chandra Rai

Different samples of pyridine and piperidine complexes with ethereal blue peroxychromic acid have been prepared and analysed, and their empirical and molecular formulae suggested.

Riesenfeld (*Ber. Naturforsch. Ges. Freiburg*, 1906, **17**, 1062) established four oxidation products representing blue peroxychromic acid: (1) mono-perchromates, $HCrO_5$, with an organic nitrogen base (blue or violet); (2) di-perchromates, RH_2CrO_7 or $RCrO_5.H_2O_2$ (blue); (3) tri-perchromates, R_3CrO_8 (red); (4) complex chromium tetroxides, $CrO_4.3NH_3$.

Wiede (*Ber.*, 1897, **30**, 2178) prepared the compounds of the type (1) and assigned the formula $RCrO_3.H_2O_2$.

Rosenheim, Hakki and Krause (*Z. anorg. allg. Chem.* 1932, **209**, 175) discussed the structure of perchromates and suggested the following structure :



Schwarz and Giese (*Ber.*, 1933, **66B**, 310; cf. *Ber.*, 1932, **65B**, 871) suggested three formulae of blue potassium perchromates: KH_2CrO_7, $KCrO_5.H_2O_2$ and $KCrO_6.H_2O_2$.

The preparation and analysis of blue, slightly soluble, explosive $TlCrO_6$ indicated that that the third formula was correct. They proposed the structural formula as double molecules $K_2Cr_2O_{12}$ containing sexivalent chromium and numerous peroxide linkages.

A further study was made by Schwarz and Elstner (*Ber.*, 1936, **69B**, 575) of the blue compound, believed by Riesenfeld and Mau (*Chem Abs.*, 1914, **8**, 1714) to be $H_3CrO_8.2H_2O$.

The formula CrO_5 was confirmed by working with the pyridine complex of the blue peroxychromic acid, and the formula for the pyridine complex was assigned to be $RCrO_5$ (where R stands for one pyridine molecule). If the formula of the pyridine complex were accepted as $RCrO_5$, the percentages of pyridine in the complex ought to have been 37.44, of chromium 24.64, and that of oxygen, 37.92. But when the percentages of pyridine, chromium and oxygen were determined from the pyridine complex in this laboratory, it came out to be between 47 and 47.3 (for pyridine), 30.04 and 30.31 (for chromium) and 22.45 and 22.91 (for oxygen). Moreover, various formulae suggested by various workers clearly indicate chromium to be always present in the acidic part of the complex. It has been observed by Rai and Prakash (*Z. anorg. allg. Chem.*, 1954, **275**, 95) that the decomposition product of the ethereal blue peroxychromic acid contains chromium in basic as well as in acidic parts. Therefore the present paper records the study of the pyridine and piperidine complexes of the ethereal blue peroxychromic acid.

The complexes of pyridine and piperidine were prepared as laid down under "Experimental". The complexes were found to be insoluble in almost all organic

solvents but soluble in caustic soda solution. When the solutions of pyridine and piperidine complexes in NaOH solution were kept for a day or so, green precipitate of chromium hydroxide were obtained. When the precipitates were filtered and the filtrates were acidified with acetic acid, and to these barium chloride and lead acetate solutions were added separately, yellow precipitates of barium chromate and lead chromate were formed. Further, the acidified solutions of the filtrates also liberated iodine from KI solution. These qualitative tests prove that chromium is present in the basic as well as in acidic parts of the complexes.

EXPERIMENTAL

Preparation and Examination of Pyridine and Piperidine Complexes.—Blue peroxychromic acid was prepared by taking 5% chromic acid solution (800 c.c.) to which 450 c.c. of ether was added. The mixture was cooled in ice and to it 320 c.c. of 20 vol. H_2O_2, also cooled in ice, added. The blue peroxychromic acid was formed which on shaking dissolved in ether. The aqueous layer was separated in a separating funnel. The ethereal layer of blue peroxychromic acid was taken at the temperature of ice in a flask and made up to 500 c.c. with ether, and kept in ice.

The ethereal blue peroxychromic acid (50 c.c.) was taken in a number of Erlenmeyer flasks and varying volumes of pyridine and piperidine were added separately. After keeping these overnight the complexes were found to be precipitated from ethereal solutions.

The above precipitates were filtered separately and washed with 5% alcoholic solution till no yellow coloration was obtained, and then finally washed with ether and dried in a desiccator. Different samples were analysed separately.

Sample No. (50 c.c. each)	...	A	B	C	D
Pyridine (added in c.c.)	...	25	50	75	100
Piperidine (added in c.c.)	...	25	50	75	100

Estimation of Total Chromium.—Definite masses of the pyridine and piperidine complexes were taken separately in weighed silica crucibles and heated at first slowly and then strongly. The complexes on heating decomposed to Cr_2O_3. These were weighed which gave the weight of Cr_2O_3. Care was taken in heating the complexes as these were highly explosive.

Determination of the Oxidation Values of the Pyridine and Piperidine Complexes in NaOH *solution in terms of volumes of N/20 Sodium Thiosulphate soln. by Iodimetry.*—Definite masses of pyridine and piperidine complexes were dissolved separately in 5 c.c. of *N*-NaOH solution and each solution was made up to 100 c.c.

The solutions (25 c.c. each) were taken and added to aqueous sotutions of KI and were acidified with H_2SO_4 (dil.) till distinctly acidic. Iodine was liberated which was titrated with the standard hypo solution using starch as indicator.

Estimation of Chromium in the Basic part as well as Oxidation Values of Filtrates in terms of volume of N/20 Sodium Thiosulphate solution.—From the above 100 c.c. solutions, 25 c.c. aliquots were separately taken in beakers and kept in a bath of

boiling water till green chromium hydroxide was completely precipitated. These were filtered over gravimetric filter papers and washed with hot water till the precipitates were free from NaOH and chromate ions. The precipitates were then ignited in weighed silica crucibles and weighed as Cr_2O_3. This gave the amounts of chromium oxide corresponding to the amounts of chromium in the basic parts of the two complexes.

The filtrates were taken along with wash water and made distinctly acidic with H_2SO_4 (dil.) and titrated iodimetrically with $N/20$ sodium thiosulphate solution using starch as indicator.

Estimation of Nitrogen or Pyridine and Piperidine.—This was carried out by Dumas' method. The percentage of nitrogen as well as of pyridine and piperidine are presented in Table I.

TABLE I

Sample No.	% Nitrogen.	% Pyridine or piperidine.	% Total Cr.	% Cr in the basic part.	$N/20$ Hypo reqd.	$N/20$ Hypo used for the filtrate.
			A. Pyridine complex.			
A	8.36	47.17	30.20	15.20	21.70 c.c.	21.40 c.c.
B	8.40	47.30	30.25	15.07	21.50	21.60
C	8.34	47.05	30.04	15.15	21.60	21.40
D	8.35	47.00	30.31	15.17	21.50	21.60
			B. Piperidine complex.			
A	9.88	59.90	22.00	11.20	14.50	14.60
B	9.84	59.80	22.50	11.30	14.40	14.50
C	9 88	59.90	22.60	11.25	14.60	14 40
D	9.88	59.90	22.60	11.30	14 50	14 40

From the above table the empirical formula for the pyridine complex is found to be $RCrO_{2.5}$ or $R_2Cr_2O_5$ and for the piperidine complex, $R_{1.5}CrO_{2.5}$ or $R_3Cr_2O_5$ (where R stands for one molecule of organic bases).

CONCLUSION

It is quite clear from the above table that the chromium is present in the acidic as well as in basic part of the complexes in equal proportions. Therefore considering the above data and the chemical properties of the complexes, the molecular formula for the pyridine complex may be written as (*a*) $R_2Cr(CrO_5)$, (*b*) $R_4Cr_2(Cr_2O_{10})$ or (*c*) $R_4Cr_2(CrO_5)_2$; and for the piperidine complex as (*a*) $R_3Cr(CrO_5)$, (*b*) $R_6Cr_2(Cr_2O_{10})$ and (*c*) $R_6Cr_2(CrO_5)_2$. It is important to note that the number of molecules of piperidine is greater than those of pyridine in the corresponding complexes in contrast to the observations of the previous workers (Wiede, *loc. cit.*) who mentioned similar complexes with pyridine and piperidine.

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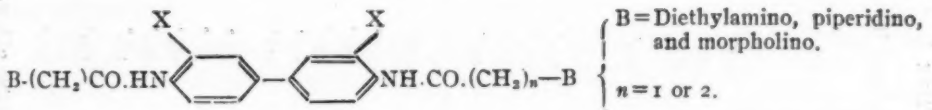
SEARCH FOR NEW LOCAL ANAESTHETICS. PART III

By I. Sen Gupta, K. S. Narang, O. P. Vig and P. C. Bansal

Several *bis*-diethylamino-, piperidino- and morpholino-acetyl and -propionyl derivatives of benzidine, tolidine and dianisidine have been synthesised and their local anaesthetic activity studied.

A series of local anaesthetics containing diphenyl nucleus have been reported by Braker and Christiansen (*J. Amer. Pharm. Assoc.*, 1935, **24**, 358) and some of these compounds have been found more active than procaine and cocaine. Strong local anaesthetic activity has also been reported in the case of dibasic esters containing diphenyl nucleus (Case and Koft, *J. Amer. Chem. Soc.*, 1941, **63**, 508; Roberts and Johnson, *ibid.*, 1925, **47**, 1396). 2:2′-Diaminodiphenyl also shows local anaesthetic activity, about quarter the activity of cocaine (Chierici, *Ann. chim. farmac.*, 1938, 48). The present work was undertaken to synthesise dibasic anilides of the general formula (I), containing diphenyl nucleus as lipolytic moiety.



(I)

These compounds have two anaesthesiophoric groups attached to two benzene nuclei in diphenyl. The presence of methyl or methoxy group, *ortho* to the aneasthesiophoric group, is conducive to local anaesthetic potency (Lofgren, *Chem. Abs.*, 1937, **31**, 7854).

For the synthesis of these compounds, the chloro-acylated derivatives of benzidine, *o*-tolidine and *o*-dianisidine were prepared by treating the base with chloroacetyl chloride or β chloropropionyl chloride. The resulting compound was condensed with the secondary amine. The bases were smoothly converted into their hydrochlorides.

Experimental

1. NN′-bis-*Chloroacetylbenzidine*.—Chloroacetyl chloride (22.6 g.) in dry benzene (50 c.c.) was added in small lots to a cooled solution of benzidine (28.4 g.), finely suspended in dry benzene (150 c.c.). The reaction mixture was thoroughly shaken. It was refluxed for 3 hours on a water-bath. Benzene was distilled off and the residue decomposed with ice-cold water. A yellow powdery mass was obtained which was washed with HCl (dil.) and then several times with water. It was crystallised from alcohol, yield 39.6 g., m.p. 330°. (Found: N, 8.5. $C_{16}H_{14}O_2N_2Cl_2$ requires N, 8.3 %).

TABLE I

[B, T and D stand respectively for benzidine, *o*-tolidine and *o*-dianisidine].

No.	Compounds.	Solvent for crystallisation.	M. P. of the (compound).	M. P. of the (hydrochloride)	Mol. formula of the compound.	Analysis of the compound. Found.	Calc.
3.	NN'-*bis*-(N-piperidinoacetyl)-B	* Pet. ether	208°	278-80°	$C_{26}H_{34}O_2N_4$	N: 12.8%	12.9%
4.	,, (N-morpholinoacetyl)-B	EtOH	208°	270°	$C_{24}H_{30}O_4N_4$	N: 12.4	12.7
5	,, (β-chloropropionyl)-B	,,	265°	...	$C_{18}H_{18}O_2N_2Cl_2$	N: 7.82	7.67
6.	,, (β-diethylaminopropionyl)-B	Pet. ether (40°-60°)	186°	298°	$C_{26}H_{38}O_2N_4$	N: 13.5	13.0
7.	,, (β-N-piperidino- ,,)-B	*Pet ether	223°	325°	$C_{25}H_{36}O_2N_4$	C: 72.85 H: 7.95 N: 11.8	72.72 8.28 12.11
8.	,, (β-N-morpholinopropionyl)-B	EtOH	235°	330°	$C_{25}H_{34}O_4N_4$	N: 11.4	12.01
9.	,, (chloroacetyl)-T	,,	285°	...	$C_{18}H_{18}O_2N_2Cl_2$	N: 7.6	7.67
10	,, (diethylaminoacetyl)-T	,,	160°	281°	$C_{28}H_{38}O_2N_4$	N: 12.3	12.78
11.	,, (N-piperidino ,,)-T	,,	197°	235°	$C_{28}H_{38}O_2N_4$	C: 72 4 H: 8.0 N: 12.1	72.7 8.28 12.11
12.	,, (N-morpholinoacetyl)-T	,,	228°	268°	$C_{24}H_{34}O_4N_4$	N: 12.23	12.66
13.	,, (β-chloropropionyl)-T	,,	228°	...	$C_{20}H_{22}O_2N_2Cl_2$	N: 6.9	7.12
14.	,, (β-diethylaminopropionyl)-T	,,	156°	305°	$C_{28}H_{42}O_2N_4$	N: 11.9	12.01
15.	, (β-N-piperidino ,,)-T	,,	177°	290°	$C_{30}H_{42}O_2N_4$	N: 11.4	11.42
16.	,, (β-N-morpholino ,,)-T	*Pet. ether	222°	265°	$C_{28}H_{38}O_4N_4$	N: 11.3	11.35
17.	,, (chloroacetyl)-D	Dilute alcohol	214°	...	$C_{16}H_{18}O_4N_2Cl_2$	N: 6.99 Cl: 17.3	7.05 17.80
18.	,, (diethylamino-acetyl)-D	Benzene	149°	213°d	$C_{26}H_{38}O_4N_4$	N: 12.2	12.12
19.	,, (N-piperidino- ,,)-D	,,	210°	267°d	$C_{28}H_{38}O_4N_4$	N: 11.3	11.33
20.	,, (N-morpholino- ,,)-D	*Pet. ether	262°	> 300°	$C_{26}H_{34}O_6N_4$	N: 11.49	11.24
21.	,, (β-chloropropionyl)-D	EtOH	223°	...	$C_{20}H_{22}O_4N_2Cl_2$	N: 6.42	6.50
22.	,, (β-diethylaminopropionyl)-D	,,	165°	210°	$C_{28}H_{42}O_4N_4$	N: 11.2	11.24
23.	,, (β-N-piperidino- ,,)-D	Benzene	190°	232°	$C_{30}H_{42}O_4N_4$	C: 68.3 H: 7.8	68.9 8.0
24.	,, (β-N-morpholino- ,,)-D	,,	223°	252°	$C_{28}H_{38}O_6N_4$	N: 10 8	10.64

* Pet ether refers to petroleum ether of b. p. 80°-100°.

2. NN'-bis-(*diethylaminoacetyl*)-*benzidine*.—A mixture of diethylamine (2.92 g., 0.04 *M*) and the above chloro compound (4.37 g., 0.01 *M*) in absolute alcohol (30 c.c.) was refluxed for 5 hours. Alcohol was distilled off and the residue washed with sodium bicarbonate solution, followed several times with water. The product was dried and crystallised from petroleum ether (80°-100°), m.p. 131-32°, yield 2.8 g. (Found: C, 70.2; H, 8.04; N, 13.9. $C_{24}H_{34}O_2N_4$ requires C, 70.23; H, 8.26; N, 13.68 %).

Hydrochloride of the above base was prepared by passing dry HCl gas in absolute alcoholic solution of the base. Alcohol was distilled off and the hydrochloride was crystallised from acetone, m.p. 274-75°.

The other analogues prepared similarly are shown in Table I.

Compounds No. 10, 11 and 16 have been tested for local anaesthetic activity at the Central Drug Research Institute, Lucknow. These showed no surface anaesthesia when applied to the cornea of guinea pigs in 3% solution. For intradermal anaesthesia, in 2% solution in normal saline, the action of these compounds started after one minute in each case and lasted for 75, 35 and 50 minutes respectively. The diethylamino compound (No. 10) shows a better activity than piperidino analogue (No. 11). The compounds in the series are being further studied for their pharmacological activity.

The authors wish to thank the Director, Central Drug Research Institute, Lucknow, for the pharmacological tests of the compounds.

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* Pet ether refers to petroleum ether of b. p. 80°-100°.

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SHORT NOTES

REDUCTION OF VANADIUM SALTS BY NASCENT HYDROGEN FROM HYDROCHLORIC ACID AND METALS: MAGNESIUM, ZINC AND CADMIUM

By B. S. Srikantan

Mellor ("Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. I, p. 334, Longmans, 1920) summarises the theories on nascent hydrogen by saying "that the so-called nascent hydrogen is assumed to consist of electrically neutral atoms (mono) of hydrogen and the difference in the nascent hydrogen derived from different sources is due to the effective concentration of mono-atomic hydrogen which in turn is determined by the rate of conversion of the mono-atomic into ordinary hydrogen." In a previous communication (this *Journal*, 1951, **28**, 69) it was shown that the rate of reduction of $KMnO_4$ by nascent hydrogen from Zn- H_2SO_4 was twice as fast as that from Cd-H_2SO_4, and the rate of production of nascent hydrogen from Zn-H_2SO_4 was concluded to be twice that from Cd-H_2SO_4. Tommasi (*Ber.*, 1898, **31**, 345, 1878; *Chem. News*, 1879, **40**, 245; *J. Phys. Chem.*, 1897, **1**, 555) pointed out the inability to explain why Zn-HCl reduced salts of vanadium pentoxide to dioxide stage, while Mg-HCl reduced only to trioxide stage under similar conditions. Magnesium precedes zinc in E.M.F. series, but the order of activity in the reduction of V_2O_5 in HCl is reverse. In this note the observations of Tommasi on the reduction of V_2O_5 have been repeated with Mg, Zn and Cd, and an explanation for the order of nascent activity of hydrogen from these metals and acid in the reduction of V_2O_5 is put forward.

Pure vanadium pentoxide was dissolved in hot HCl (conc.) to a clear solution, and diluted. Pure metals, viz., Zn, Cd and Mg, almost with equal surfaces, were put into the solution and kept shaken. After complete reduction in each case, the colour of the solution was noted. Of these, zinc reduced the yellow solution to a lavender colour; Mg, though evolved hydrogen rapidly and went into solution, could reduce it only to the green V_2O_3 stage. The results are tabulated below.

TABLE I

Stages of oxides of vanadium.	Corresponding chlorides.	Colour of salt solution.	Metals giving reduction to stage.
V_2O_5	$VOCl_3$	Yellow	...
VO_2	$VOCl_2$	Blue	Cd
V_2O_3	VOCl	Green	Mg
V_2O_2	VCl_2	Lavender	Zn

The order of decreasing activity of nascent hydrogen is from Zn-Mg to Cd.

The production of neutral hydrogen atoms from hydrogen ions involves the ionisation of the metal by transfer of electric charges.

$$M + 2H^+ \rightarrow 2H + M^{2+}$$

Therefore the production of nascent hydrogen and its activity are the function of the ionisation potential of the particular metal. The following table records the second ionisation potential (e) and the ionic radii (r) of Mg, Zn and Cd from Pauli.

TABLE II

Metal.	e.	r.	e/r.
Zn	17.89 volts	0.74Å	24.2
Mg	14.96	0.65	23.0
Cd	16.84	0.97	17.3

It is seen from the above table that the value of e/r for these metals are in the order of Zn-Mg and Cd, which is also the order of reduction of V_2O_5 in HCl by these metals. Therefore it can be concluded that the nascent activity of hydrogen from different sources is a function of ionisation potential and the ionic radii of the metals generating the hydrogen. e/r has the dimensions of force and may be termed "field intensity".

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USE OF THIAZOLIDONES AND 5-AMINOTHIAZOLIDONES AS ANALYTICAL REAGENTS FOR COPPER AND SILVER

BY BIRENDRA KUMAR PATNAIK

In course of our investigations on "thiazolidone compounds", it was considered of interest to study all their possible applications in analytical procedures, viz., for the estimation of silver (Das and Rout, *J. Sci. Ind. Res.*, 1955, **14B**, 16). Another compound of the same series has been examined here for its use in the estimation of copper. One of another type of thiazolidone derivatives, viz., 5-amino-2-*p*-nitrophenylimino-4-thiazolidone, has also been studied for the estimation of silver.

Estimation of Copper.—The reagent, 2-*p* tolylimino-4-thiazolidone, was prepared by refluxing *p*-tolylthiourea and monochloroacetic acid in absolute alcohol using anhydrous sodium acetate as the condensing agent. Stock solutions of copper sulphate were prepared and were estimated by the iodimetric method. The reagent being insoluble in water, a solution of the reagent in minimum volume of alcohol was employed.

To a known volume of the standard $CuSO_4$ solution, maintained at p_H 5.2 by adding 100 c.c. NaAc-HAc buffer, an excess of the warm alcoholic solution of the reagent (2%) was added dropwise with constant stirring till complete precipitation. The complex formed was slightly warmed for about 5 minutes on a water-bath and allowed to stay overnight. Some of the reagent came down along with the complex that had precipitated. This could not, however, be removed by any of the solvents or solvent mixtures without affecting the weight of the complex. Hence, the precipitate was

filtered through a Whatman 42 filter paper. The precipitate was next dried and ignited in a tared porcelain crucible to a constant weight.

TABLE I

CuO calc.	CuO found.	Error.
0.0976 g.	0.0976 g.	±0
0 0936	0.0934	−0.0002 g.
0 0858	0.0856	−0.0002

The complex when analysed gives the following results: C, 50.33% ; H, 3.42% ; N, 11.46% ; Cu, 13.23 %. These point to the molecular formula given below for the complex. The proposed formula $Cu(C_{10}H_9ON_2S)_2$ requires C, 50.68 ; H, 3.80 ; N, 11.82 ; Cu, 13.39%.

Estimation of Silver.—The reagent, 5-amino-2-*p*-nitrophenylimino-4-thiazolidone, was prepared by the cleavage of the azo group in 5-phenylazo-2-*p*-nitrophenylimino-4-thiazolidone which was prepared by coupling diazotised aniline with 2-*p*-nitrophenylimino-4-thiazolidone.

Stock solutions of the salt ($AgNO_3$) were prepared and were estimated by titrating with standard thiocyanate solutions using ferric alum as indicator. The amino compound being insoluble in water, its alcoholic solution was used.

To the $AgNO_3$ solution (containing 0.5966 g. $AgNO_3$), maintained at p_H 5.2 (by adding 50 c.c. of acetate buffer), 0.95 g. of the reagent in 15 c.c. warm alcohol was added dropwise with constant stirring. The complex formed was warmed at 60° for about 10 minutes, kept overnight and filtered through a previously weighed (Gooch) No. 4 crucible. The precipitate was washed with 20% warm alcohol. The complex was dried at 105° and weighed.

TABLE II

Ag present in soln.	Wt. of the complex calculated on the basis of the formula proposed.	Wt of the complex found.
0.05966 g.	0.1263 g.	0.1260 g.
0 05966	0 1263	0 1259
0.05966	0.1263	0.1261

Composition of the Silver Complex.—A known amount of the silver complex was taken in a weighed porcelain crucible and heated till the organic contents were burnt away. The crucible was then heated to red heat for about half an hour, cooled and the contents weighed.

TABLE III

Ag present in soln.	Wt. of complex.	Ag found.
0.0312 g.	0.1042 g.	0.0310 g.
0.0292	0.0974	0.0289

The above results lead to the conclusion that the silver complex formed will be formulated as $Ag(C_9H_7O_3N_4S)$.

The complex when analysed gives the following results: C, 29.67% ; H, 1.68% ; N, 15.23% ; Ag, 29.78%. These point to the formula given above for the complex. The proposed formula requires C, 30.08 ; H, 1.94; N, 15.59 ; Ag, 30 08%.

The author expresses his sincere thanks to Dr. M. K. Rout, Reader in Chemistry, Ravenshaw College, for suggesting the problem and for his constant guidance and to the Board of Scientific and Industrial Research, Orissa, for research grants to carry out this investigation.

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BEHAVIOUR OF CHLORONITROBENZENES WITH HYDRAZINE AND HYDRAZINE DERIVATIVES: HYDRAZOBENZENES

BY SHIAM SUNDER JOSHI AND DALEEP SINGH DEORHA

Interaction between a benzene derivative having a reactive halogen atom, viz., picryl chloride, and phenylhydrazine was employed by Fischer (*Annalen*, 1887, **190**, 132) to prepare 2 : 4 : 6-trinitrohydrazobenzene. Subsequently, by reacting benzene derivatives having a labile halogen atom with phenylhydrazine and substituted phenylhydrazines, Willgerodt and collaborators (*Ber.*, 1891, **24**, 1661 ; *J. prakt. Chem.*, 1882, *ii*, **37**, 351 ; 1891, **43**, 490 ; 1891, **44**, 72, 452) obtained 2′-chloro-, 3′-chloro- and 4′-chloro-2 : 4 : 6-trinitro-, -2 : 4-dinitro-, 3′-chloro-, 4′-chloro- and 4′-bromo-2 : 4-dinitrohydrazobenzenes. Werner and co-workers (*Ber.*, 1899, **32**, 3266) prepared 2 : 4 : 2′-trinitro-, 2 : 4 : 3′-trinitro- and 2 : 4 : 4′-trinitro-hydrazobenzenes.

Giua and co-workers (*Gazzetta*, 1918, **48**, 8 ; 1921, **51**, 307 ; 1922, **52**, 346 ; 1923, **53**, 165 ; *Atti R. Acad. Lincei*, 1918, *v*, **27**, 379) and Mangini (*Gazzetta*, 1935, **65**, 1191) prepared by substitution of a labile nitro group some derivatives of hydrazobenzene, such as, 5-chloro-2 : 4-dinitro-, 5-bromo-2 : 4-dinitro-, 5-chloro-2 : 4′-dinitro-, -4 : 6-dinitro-3-methyl-, -2:6-dinitro-3-methyl-, 5-chloro-2 : 4′-dinitro-, 4 : 6-dinitro-2′ : 3-dimethyl- and 4 : 6-dinitro-3 : 4′-dimethyl-hydrazobenzenes.

During the present investigations some substituted hydrazobenzenes have been prepared by keeping polynitro compounds having a labile halogen atom with phenylhydrazine (1 : 2) in alcohol at room temperature (15°-20°) for 3 to 4 days. 3-Chloro-4 : 6-dinitro-, 2-chloro-4 : 6-dinitro-, 2-bromo-4 : 6-dinitro-, 4 : 6-dinitro-3-methyl-, 4 : 6-dinitro-2-methyl-, 2 : 4 : 6-trinitro-3-methyl-hydrazobenzenes have been obtained from 1-chloro-3-bromo-4 : 6-dinitro-, 1 : 2-dichloro-4 : 6-dinitro-, 1-chloro-2-bromo-4 : 6-dinitro-, 1-chloro-4 : 6-dinitro-3-methyl-, 1-chloro-4 : 6-dinitro-2-methyl- and 1-chloro-2 : 4 : 6-trinitro-3-methyl-benzenes and phenylhydrazine in this way.

Attempts to prepare the corresponding hydrazobenzenes from 1 : 4-dichloro- and 1 : 4-dibromo-2 : 6-dinitrobenzenes were not successful. These compounds and phenylhydrazine even in dilute alcoholic solutions afford on keeping for one hour the corresponding 6-halogeno-4-nitro-2-phenylbenzotriazoles This can be attributed to the ease with which their hydrazobenzenes cyclise.

On the other hand, 6-chloro-1-bromo-2 : 4-dinitro-3-methyl-, 1 : 6-dibromo-2 : 4-dinitro-3-methyl-, 4-chloro-1-bromo-2 : 6-dinitro-3-methyl- and 1 : 4-dibromo-2 : 6-dinitro-3-methyl-benzenes and phenylhydrazine do not react at room temperature on keeping for several days. Even when their solutions in absolute alcohol are boiled the reaction takes place to a small extent, affording only the corresponding 2-phenylbenzotriazoles in poor yields. Hydrazobenzene derivatives could not be isolated in any case.

Hydrazobenzenes.—Alcoholic solutions of the reactive halogen compounds and phenylhydrazine (1 : 2) were kept at room temperature (15°-20°) for four days. The hydrazobenzenes separated in crystalline forms. These were crystallised from benzene.

Hydrazobenzenes obtained from different reactive halogen compounds together with their characteristics are shown below.

Halogeno-nitrobenzene used.	Hydrazobenzene formed.	% Yield.	M.P.	Colour.	Formula.	Found.	Calc.
1-Chloro-3-bromo-4 : 6-dinitro-	* 3-Chloro-4 :6-dinitro-	56	170°	Orange	$C_{12}H_9O_4N_4Cl$	Cl, 11.36	11.50%
1 : 2-Dichloro-4 :6-dinitro-	2-Chloro-4 :6-dinitro-	58	168°	Fawn	$C_{12}H_9O_4N_4Cl$	Cl, 11.43	11.50
1-Chloro-2-bromo-4 :6-dinitro-	2-Bromo-4 :6-dinitro-	60	169°	Yellow	$C_{12}H_9O_4N_4Br$	Br, 22.51	22.66
1-Chloro-4 :6-dinitro-3-methyl-	*4 :6-Dinitro-3-methyl-	50	157°	Do	$C_{13}H_{12}O_4N_4$	N, 19.68	19.44
1-Chloro-4 :6-dinitro-2-methyl-	4 :6-Dinitro-2-methyl-	54	154°	Orange-yellow	$C_{14}H_{12}O_4N_4$	N, 19 14	19.44
1-Chloro-2 :4 :6-trinitro-3-methyl-	2 :4 :6-Trinitro-3-methyl-	55°	149°	Orange	$C_{13}H_{11}O_6N_5$	N, 20 73	21.02

* Prepared before by other methods.

The hydrazobenzenes are yellow to orange in colour and are easily soluble in common organic solvents in cold. They readily cyclise ; on boiling in alcohol they yield 2-phenylbenzotriazole derivatives, while in acetic acid they form 2-phenylbenzotriazole-1-oxides.

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THE BASIC CONSTITUENTS OF GAS-TAR

By S. K. Saha

In search for a source of β-and γ-picoline, *the basic fraction* of the light oil of the tar supplied by the Oriental Gas Company, Calcutta, was subjected to fractional distillation in a specially devised double Gan's column (1 m. long). The fraction boiling at 90°-170° was fractionated repeatedly until constant fractions were obtained. In all 12 fractionations were made. From 5 gallons of crude pyridine, 18 lbs. of pyridine (112°-118°), 6 lbs. of α-picoline (126°-132°), 8 lbs. of β-picoline (140°-147°), 4 lbs. of 2:4-lutidine (152°-158°), 8 lbs. of a residue boiling above 160° and about 6 lbs. of total intermediate fractions were obtained.

The β-picoline fraction usually contains a mixture of β-picoline, γ-picoline and 2:6-lutidine. Attempts were therefore made to separate the constituents by employing methods based on the difference in solubility of the complex salts formed by oxalic acid (Lidstone, *J. Chem. Soc.*, 1940, 241) and zinc chloride (*Annalen*, 1920, **420**, 192, 197; U. S. P. 2, 456, 773/1948; *Chem. Abs.*, 1949, **43**, 2240). No trace of γ-picoline or 2:6-lutidine could be obtained after repeated trials. The "β-picoline" fraction was then oxidised by potassium permanganate when nicotinic acid (m. p. 228°) was obtained in a fairly good yield. It is concluded that the β-picoline fraction from gas tar does not contain any γ-picoline nor any 2:6-lutidine. Attempts were next made to oxidise 2:4-lutidine fraction into 2:4-lutidinic acid and to convert the latter into 4-pyridine carboxylic acid or *iso*nicotinic acid

Oxidation of "β-Picoline" fraction by $KMnO_4$.—A mixture of the "β-picoline" fraction (200 g.) and water (2½ litres) was heated on the water-bath under reflux and stirred while powdered $KMnO_4$ (900 g.) was added in portions of 20 g. during 6 hours. After the last charge of the permanganate had been decolorised, the hot reaction mixture was filtered by suction. The manganese dioxide was washed twice with hot water. The combined filtrate was concentrated to 3000 c.c. and set at p_H 3-4 with about 260 c.c. of HCl. The slurry was heated up to 95°-100° to dissolve the voluminous precipitate and allowed to cool slowly at room temperature. The purpose of slow cooling was to avoid contamination with potassium chloride. The nicotinic acid, thus obtained, was filtered off and washed with a little cold water. The filtrate was again concentrated and cooled to 5°, when a second crop of nicotinic acid was obtained. Total yield was 60%.

Oxidation of 2:4-Lutidine fraction by $KMnO_4$ *to 2:4-Lutidinic Acid and Conversion to* iso*Nicotinic Acid.*—2:4-Lutidine fraction (100 g.) was heated on a water-bath and stirred with a solution of $KMnO_4$ (300 g.) in 2000 c.c. water till the colour was discharged (6 hours). A further equal amount of $KMnO_4$ in 500 c.c. water was then added and the heating continued till the liquid again was decolorised (12 hours). The reaction mixture was filtered hot. The precipitate of manganese dioxide was twice washed with hot water and filtered. The combined filtrate was evaporated to 1/3

volume, acidified to litmus with H_2SO_4 (dil.) and evaporated to crystallisation. An equal volume of alcohol was then added. The filtrate from the precipitated potassium sulphate was diluted with water (1000 c.c.) and warmed, and 2 : 4-lutidinic acid precipitated as the silver salt by addition of dilute silver nitrate solution. The precipitate was washed with warm water, suspended in hot water and decomposed by H_2S. 2 : 4-Lutidinic acid separated from the filtrate on evaporation, followed by cooling. The dried acid was heated above its melting point under diminished pressure (250 mm.) when there was a rapid evolution of carbon dioxide and *iso*nicotinic acid sublimed on the upper part of the flask ; m. p. 317°, yield 50 g.

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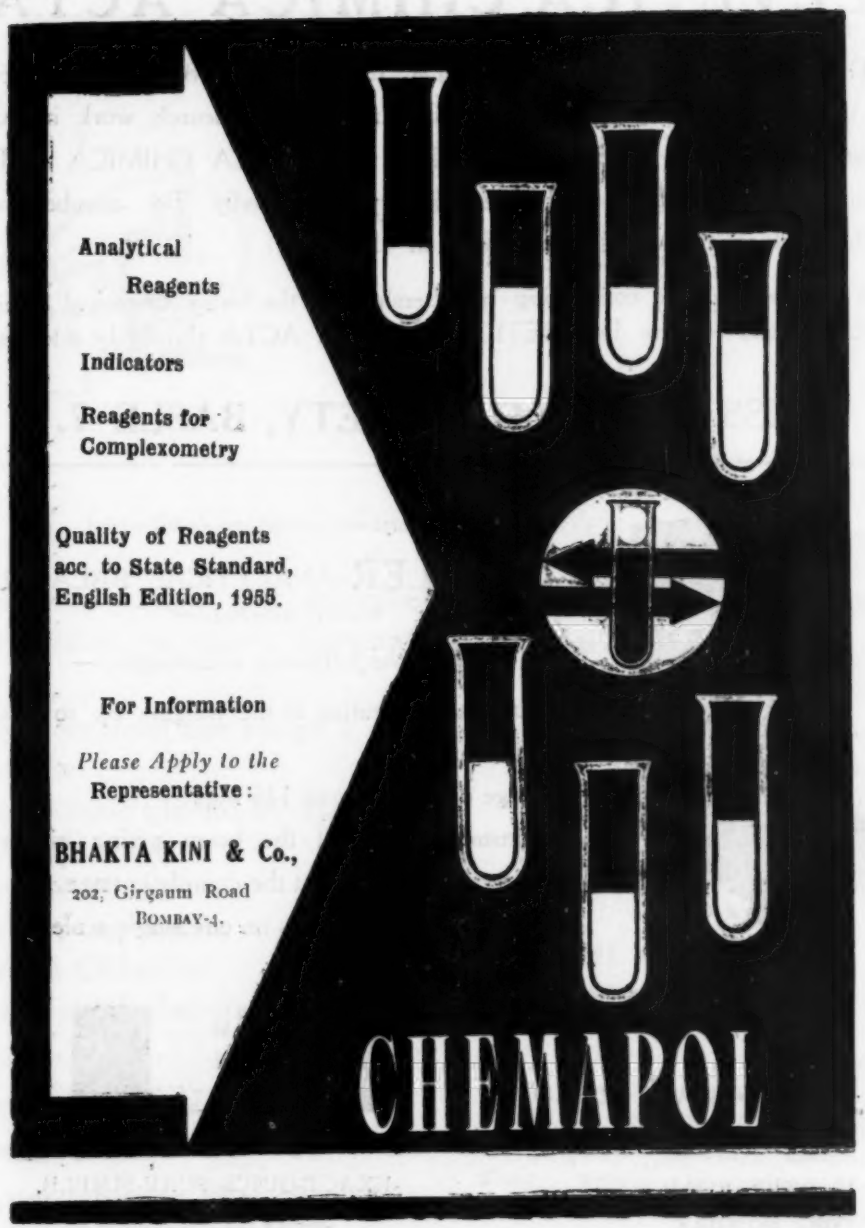

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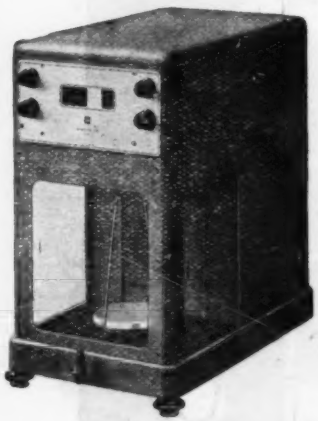

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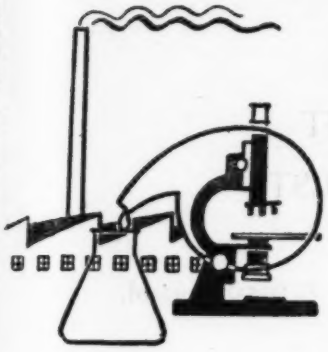

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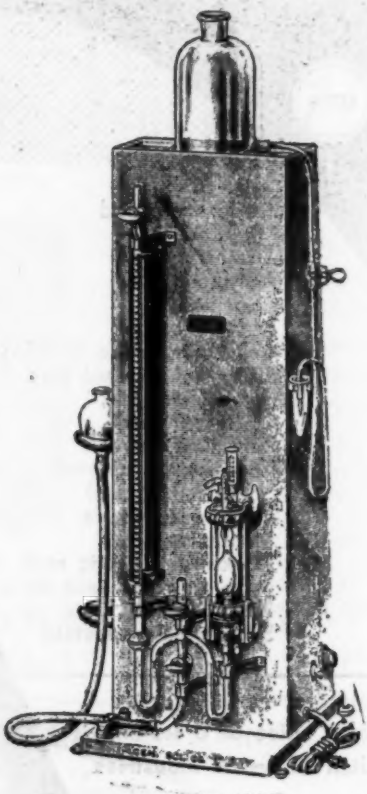

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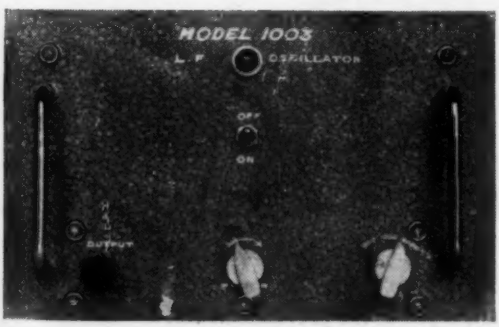

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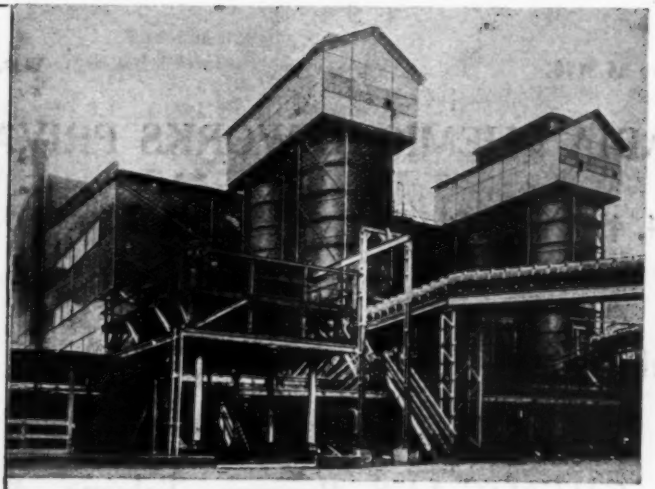

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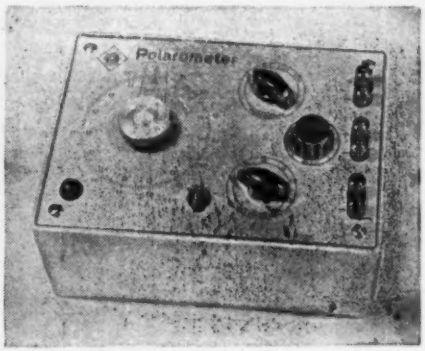

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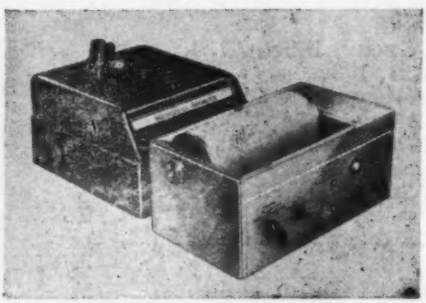

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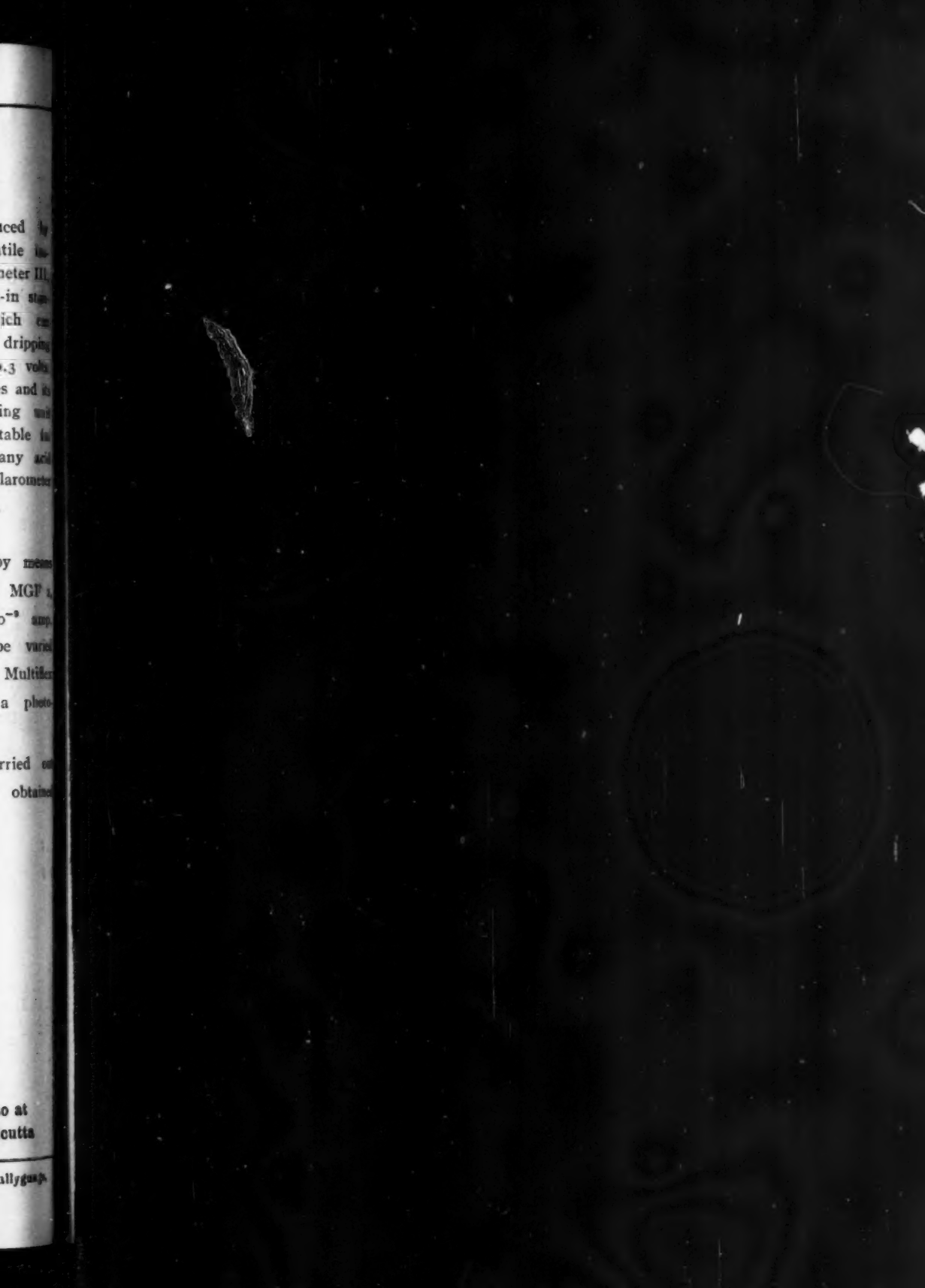
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